PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2001-018290
(43)Date of publication of application : 23.01.2001

(51)Int.Cl. B29C 55/12
B32B 27/36
B65D 1/09
// B29C 49/02
B29K 67:00
B29L 7:00
B29L 9:00

(21)Application number : 11-193585
(22)Date of filing : 07.07.1999

(71)Applicant : TOYO SEIKAN KAISHA LTD
(72)Inventor : ITO TAKURO
YAMAGUCHI YUJI
WATANABE SUKETAKA
ARITA TSUNEO

(54) ALIPHATIC POLYESTER STRETCH-MOLDED OBJECT AND PRODUCTION THEREOF

(57)Abstract:
PROBLEM TO BE SOLVED: To produce a biaxially stretched molded object made of aliphatic polyester eliminated or reduced in the anisotropy of mechanical strength characteristics and enhanced in gas barrier properties.
SOLUTION: In a method for producing an aliphatic polyester stretch-molded object by the biaxial stretch molding of a preform of a resin based on aliphatic polyester, a negative gradient is provided to a stretching speed in the biaxial stretching of the preform so that an initial stretching speed becomes high and a final stretching speed becomes low. By vapor-depositing hard carbon film, gas barrier properties are also enhanced.

LEGAL STATUS

[Date of request for examination]	09.05.2002
[Date of sending the examiner's decision of rejection]	
[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]	
[Date of final disposal for application]	
[Patent number]	
[Date of registration]	
[Number of appeal against examiner's decision of rejection]	
[Date of requesting appeal against examiner's decision of rejection]	

CLAIMS

[Claim(s)]
[Claim 1] The process of the drawing Plastic solid characterized by preparing negative inclination in a drawing rate and fabricating biaxial stretching of a preforming object at it in the process of the aliphatic series polyester drawing Plastic solid which consists of carrying out biaxial-stretching shaping of the preforming object of the resin which makes aliphatic series polyester a subject so that the drawing rate of a telophase may become [an early drawing rate] large small.
[Claim 2] The process of the drawing Plastic solid characterized by forming the hard carbon film in one [at least] front face of the aliphatic series polyester drawing Plastic solid formed with chemical vapor deposition.
[Claim 3] It is the drawing Plastic solid formed from the resin which makes aliphatic series polyester a subject, and is the following type (1).
T45 <=Tx -- (1)
the aliphatic series polyester drawing Plastic solid which Tx is the **** yield point reinforcement (MPa) of the direction of biaxial stretching of a Plastic solid among a formula, and is characterized by coming out and T45 having the strength property which is the **** yield point reinforcement (MPa) of the direction of 45 degree, and which is expressed to the drawing direction of a Plastic solid.
[Claim 4] The following type (2)
Do=(S-Sa)/S -- (2)
the drawing Plastic solid according to claim 3 characterized by the orientation degree of crystallinity (Do) which S expresses the chemical shift 100 when measuring a Plastic solid sample by 13C broad line NMR thru/or the peak area of 300 ppm among a formula, and expresses the peak area of the NMR spectrum when measuring Sa like [powder / of said sample / amorphous] the above, and which is come out of and defined being 0.15 or more.
[Claim 5] The drawing Plastic solid according to claim 3 or 4 with which aliphatic series polyester is characterized by a glass transition point (Tg) being aliphatic series polyester -60 degrees C or more.
[Claim 6] The drawing Plastic solid according to claim 3 or 4 characterized by aliphatic series polyester being polyhydroxy alkanoate.
[Claim 7] A drawing Plastic solid given in claim 3 thru/or any of 6 they are. [which is characterized by forming the hard carbon film in one / at least / front face of an aliphatic series polyester drawing Plastic solid]
[Claim 8] The container characterized by consisting of a drawing Plastic solid given in any [claim 3 thru/or] of 7 they are.

[Translation done.]

* NOTICES *

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the drawing Plastic solid and its manufacture approach of the aliphatic series polyester which has improved the anisotropy of a mechanical strength.
[0002]
[Description of the Prior Art] In recent years, the amount serves as steps splenium and the solid waste which a city discharges is approaching the limitation of an abolition throughput. As one of the ringleaders of this solid waste, plastics is always pointed out.
[0003] As the ideal solution to, the degradable plastic which disappears by natural environment attracts attention. There are a photodegradable plastic from which the chain of a polymer is cut by ultraviolet rays, and a biodegradable plastic which collapses in an operation of the enzyme which bacteria and true fungi emit to the outside of the body in a degradable plastic.
[0004] However, in the case of the photodegradable plastic, by flasking-among soil processing, effectiveness cannot be expected and it has a hope from a certain thing to a biodegradable plastic also with great fear of the environmental pollution by the decomposition product.
[0005] As a biodegradable plastic, the random copolymer of aliphatic series polyester (PHA), for example, polyhydroxy butyrate, 3-hydroxy butyrate (3HB), and 3-hydroxy BARIRETO (3HV), Pori (epsilon-caprolactone) (PCL), polybutylene succinate (PBS), a polybutylene succinate horse mackerel peat (PBAS), polylactic acid (PLLA), etc. are known conventionally.
[0006]
[Problem(s) to be Solved by the Invention] However, although these aliphatic series polyester is excellent in respect of harmony with an environment, such as biodegradability, it has the trouble which must still be solved in respect of a moldability. As one example, aliphatic series polyester is inferior in the melt nature of resin, and it has the problem that shaping of direct blow and injection drawing shaping, thermostat form shaping of a sheet, etc. is difficult. For this reason, the macromolecule quantification (JP,7-205278,A) by the chain length drawing using the improvement in melting tension (JP,5-289623,A) and diisocyanate by addition of an inorganic filler, a diepoxy compound, and an acid anhydride is proposed. Moreover, generally aliphatic series polyester can raise material strength by processing by drawing shaping.
[0007]
[Problem(s) to be Solved by the Invention] Mechanical strengths of aliphatic series polyester, such as yield point reinforcement and an elastic modulus, improve by drawing like usual plastics. However, when biaxial-stretching shaping of the aliphatic series polyester is carried out, the anisotropy of a mechanical strength produces the obtained drawing moldings.
[0008] For example, it sets to the biaxial-stretching Plastic solid of aromatic polyester and polyethylene terephthalate (PET). From the yield point reinforcement of the drawing direction of a machine, i.e., the direction, (MD), and the crossing direction (TD), and MD and TD, although reinforcement with the almost equal yield point reinforcement of the direction of 45 degrees is shown As for aliphatic series

polyester like polylactic acid, the yield point reinforcement of the drawing direction of a machine, i.e., the direction, (MD), and the crossing direction (TD) is falling [MD and] from the yield point reinforcement of the direction of 45 degrees from TD.

[0009] Thus, the anisotropy of a mechanical strength has produced the biaxial-stretching Plastic solid of aliphatic series polyester, and since reinforcement becomes low by the drawing shaft orientations which reinforcement should increase especially essentially; it has the problem that the design of a Plastic solid on the strength is difficult. For example, with solid shaping containers, such as a bottle and a cup, it is suitable to take the drawing direction to container shaft orientations and a container hoop direction. In this case, it is the main point important also for prevention about the crack by buckling prevention, the crack prevention by the drop impact, expansion, contraction, or deformation to consist the mechanical strength of the field which a drawing shaft makes isotropic. However, since mechanical strengths differ also in the direction in which the reinforcement of shaft orientations or a hoop direction makes a direction 45 degrees with a drawing shaft, the reinforcement of the biaxial-stretching Plastic solid of aliphatic series polyester has not attained the desired end. It is not practical to perform drawing actuation in the direction which inclined 45 degrees from shaft orientations and the hoop direction of a container on the other hand.

[0010] And in the biaxial-stretching Plastic solid which has the anisotropy of a mechanical strength as mentioned above, on the occasion of the compression set, the inclination to often generate a crack also found a certain thing as shown in the example of a comparison.

[0011] Therefore, the object of this invention is to set to the biaxial-stretching Plastic solid formed from aliphatic series polyester, and offer the aliphatic series polyester biaxial-stretching Plastic solid whose mechanical-strength property that the anisotropy of the above-mentioned mechanical strength was canceled thru/or reduced was stable, and its manufacture approach.

[0012]

[Means for Solving the Problem] According to this invention, in the process of the aliphatic series polyester drawing Plastic solid which consists of carrying out biaxial-stretching shaping of the preforming object of the resin which makes aliphatic series polyester a subject, the process of the drawing Plastic solid characterized by drawing shaping which prepared negative inclination in the drawing rate as the drawing rate of a telophase was made small greatly [biaxial stretching / of a preforming object / rate / early / drawing] is offered. It is the drawing Plastic solid which was formed from the resin which makes aliphatic series polyester a subject again according to this invention, and is the following type (1).

$T45 <= Tx$ -- (1)

Tx is the **** yield point reinforcement (MPa) of the direction of biaxial stretching of a Plastic solid among a formula, and the aliphatic series polyester drawing Plastic solid characterized by coming out and T45 having the strength property which is the **** yield point reinforcement (MPa) of the direction of 45 degree, and which is expressed to the drawing direction of a Plastic solid is offered. The aliphatic series polyester drawing Plastic solid by this invention is the following formula (2).

$Do=(S-Sa)/S$ -- (2)

it is desirable that the orientation degree of crystallinity (Do) which S expresses the chemical shift 100 when measuring a Plastic solid sample by 13C broad line NMR thru/or the peak area of 300 ppm among a formula, and expresses the peak area of the NMR spectrum when measuring Sa like [powder / of said sample / amorphous] the above and which is come out of and defined is 0.15 or more. Moreover, a glass transition point (Tg) is aliphatic series polyester -60 degrees C or more, and the aliphatic series polyester used for this invention shows polyhydroxy alkanoate. According to this invention, the container further characterized by consisting of the above-mentioned drawing Plastic solid is offered. The hard carbon film can be formed in the drawing Plastic solid by this invention with chemical vapor deposition in order to control the gas permeability which lets a container wall pass and to prevent the sorption of the flavor component in contents.

[0013]

[Embodiment of the Invention] [Operation] this invention is based on the new knowledge of making the

drawing rate which made the drawing rate of a telophase small greatly [biaxial stretching / of an aliphatic series polyester preforming object / rate / early / drawing] canceling thru/or reducing the anisotropy of the reinforcement of a drawing Plastic solid, and selling to it with drawing shaping which established negative inclination.

[0014] That is, in this invention, it is important for canceling thru/or reducing the anisotropy of the mechanical strength of an aliphatic series polyester drawing Plastic solid by performing biaxial-stretching actuation which prepared negative inclination in the drawing rate which makes the drawing rate of a telophase small greatly [rate / early / drawing]. For example, when a drawing rate extends at a fixed rate, when a drawing rate is large, and it is which in the case of being small, the yield point reinforcement of the drawing direction is falling as compared with the yield point reinforcement of a direction (the direction of a vertical angle) by 45 degrees. On the other hand, by performing drawing shaping which prepared negative inclination in the drawing rate which enlarges an early drawing rate and makes the drawing rate of a telophase small, it is equal to the yield point reinforcement of the direction of a vertical angle, or yield point reinforcement of the drawing direction can be made larger than it. It became possible to cancel disadvantageous profit that the reinforcement of a result and the drawing direction falls.

[0015] The aliphatic series polyester drawing Plastic solid by this invention shows the strength property with which are satisfied of said formula (1). For this reason, the container which consists of a drawing Plastic solid of this invention has the advantage that the crack by expansion contraction or deformation is also prevented effectively while it is excellent in buckling-proof nature or drop-proof impact nature.

[0016] As for the drawing Plastic solid by this invention, it is desirable that the orientation degree of crystallinity (Do) defined by said formula (2) is 0.2 especially or more 0.15 or more a mechanical property, transparency, and in respect of thermal resistance.

[0017] Usually, the thermoplastic polyester guided from the dibasic acid which makes aromatic carboxylic acid a subject, and the glycol can measure the degree of crystallinity by orientation in densimetry, and the relation of the consistency and degree of crystallinity which are measured is expressed with the following type (3). Degree-of-crystallinity Xc=(rho c/rho) x{(rho-rho am)/(rho c-rho am)} x100 -- (3)

For the consistency of the sample which rho is n-heptane-4 chlorination carbon system density gradient tubing (product made from the Ikeda ****) among a formula, and is measured 20 degrees C, and rhoam, an amorphism consistency (1.335g/cm3) and rhoc are a crystal consistency (1.455g/cm3).

[0018] However, in the case of aliphatic series polyester, most consistencies are regularity and the sample to which polylactic acid etc. especially carried out orientation also of the amorphism sample to altitude cannot ask for orientation degree of crystallinity using densimetry, either.

[0019] this invention person has relation with as close chemical shift 100 when measuring aliphatic series polyester by 13C broad line NMR thru/or peak area of 300 ppm (carbonyl carbon field) as extent of the orientation of aliphatic series polyester, and found out that the amount of preferred orientation could be measured from this peak area. That is, about an aliphatic series polyester drawing Plastic solid, it asks for the area S of an NMR spectrum, and asks for the peak area Sa of the NMR spectrum when subsequently measuring like the above about the amorphous powder of this sample, and orientation degree of crystallinity (Do) is computed from said formula (2). Thus, the response of 1:1 is between the orientation degree of crystallinity (Do) and draw magnification which were called for.

[0020] Drawing 1 shows the relation between draw magnification (shaft-orientations draw magnification, area draw magnification) and the obtained orientation degree of crystallinity (Do) about the various drawing Plastic solids of aliphatic series polyester. According to drawing 1 , it turns out that the degree of orientation ********** is increasing as draw magnification increases.

[0021] By performing biaxial-stretching actuation which prepared negative inclination in the drawing rate which makes the drawing rate of a telophase small greatly [polyester / aliphatic series / rate / early / drawing] as explained above according to this invention The strength property of a drawing moldings is in the range with which are satisfied of said formula (1), it should be anisotropy-canceled, thru/or a mechanical strength should be reduced, and the point that moreover orientation degree of crystallinity

(Do) is attained for an improvement of this anisotropy in 0.15 or more fields should be noted.
[0022] (Aliphatic series polyester resin) In this invention, the thing of the arbitration of the biodegradability aliphatic series polyester resin which makes a hydroxy alkanoate unit a subject is used as aliphatic series polyester resin. This aliphatic series polyester resin should have the molecular weight which can form a film at least, and, generally it is good 10000 thru/or 300000, and for especially that number average molecular weight to be in the range of 20000 thru/or 200000. The examples of suitable aliphatic series polyester resin are polyhydroxy alkanoate or these copolymers.
[0023] As polyhydroxy alkanoate, it is the following type [** 1].

$$-[-O-\underset{R}{\overset{}{CH}}-(CH_2)_n-\overset{O}{\overset{\|}{C}}-]-$$

R is the alkyl group of a hydrogen atom, a straight chain, or branched chain among a formula. the repeating unit 3 whose n is a positive integer containing zero and which is come out of and expressed, for example, lactic-acid [R=CH, -- [ ] n= 0, LLA], 3-hydroxy butyrate [R=CH3 n= 1, 3HB], 3-hydroxy BARIRETO [R=CH2 CH3 , n= 1, 3HV], 3-hydroxy KAPUROETO[R=(CH2) 2 CH3 , n= 1, 3HC], and 3-hydroxy heptanoate [-- R= (CH2) 3 CH3 n= 1, 3HH], 3-hydroxy octanoate [R=(CH2) 4 CH3 n= 1, 3HO], 3-hydroxy nonanoate [R=(CH2) 5 CH3 , n= 1, 3HN], 3-hydroxydecanoate [R=(CH2) 6 CH3 n= 1, 3HD], gamma-butyrolactone [R=H, n= 2, BL], delta-valerolactone [R=H, n= 3, VL], epsilon-caprolactone [R=H, n= 4, CL]
The polymer which consists of one sort of ** or two sorts or more is mentioned.
[0024] this polyhydroxy alkanoate -- polylactic acid (Pori (DL-lactic acid) which exists as polylactic acid at a rate of Pori (L-lactic acid) where a configuration unit consists only of L-lactic acid, Pori (D-lactic acid) which consists only of a D-lactic acid and an L-lactic acid unit, and D-lactic-acid kind arbitration is shown.) -- you may be a homopolymer like the Pori epsilon caprolactone again, and a copolymer with other HIDOROKISHIARUKARIETO is sufficient. Moreover, you may be 3-hydroxy butyrate, and other 3-hydroxy alkanoate and the copolymer to which copolymerization of 3-hydroxy BARIRETO was carried out especially.
[0025] A glass transition point's (Tg)'s thing 30 degrees C or more is [especially the aliphatic series polyester used for this invention] desirable -60 degrees C or more. It is industrially mass-produced among these aliphatic series polyester, and acquisition is easy and polylactic acid is mentioned as aliphatic series polyester friendly also to an environment. Polylactic acid (PLLA) is resin which uses grain starches, such as corn, as a raw material, and is a polymer which makes a monomer the lactic-acid-fermentation object of starch, and L-lactic acid. It is manufactured by the ring-opening-polymerization method and direct polycondensation method of the lactide which is generally the dimer. It is decomposed with water and carbon dioxide gas by the microorganism which exists in a nature, and its attention is paid to this polymer as resin of a perfect recycle system mold by it. Moreover, the glass transition point (Tg) has the advantage of being close to Tg of about 58 degrees C and PET.
[0026] The above-mentioned aliphatic series polyester, especially polylactic acid can also be independently used for the drawing Plastic solid of this invention, and can also be used for it also as other aliphatic series polyester, a blend object with other resin, or a layered product with other resin.
[0027] Furthermore, as other usable resin, barrier resin, for example, the hydroxyl-group content thermoplastics in which barrier nature is shown to oxygen, Nylon, barrier nature polyester resin, a high nitrile resin, the annular olefin system copolymer in which barrier nature is shown to a steam can be mentioned in a blend object with the above-mentioned aliphatic series polyester, or the form of a layered product. The resin of arbitration can be used, as long as hydroxyl-group content resin is desirable in respect of biodegradability and thermoforming is possible also among these. This resin has the repeating unit which has a hydroxyl group in that chain, and the unit which gives thermoforming nature to resin. Although hydroxyl-group content repeating units may be a vinyl alcohol unit and a hydroxyalkyl (meta) acrylate unit, in respect of biodegradability, a vinyl alcohol unit is desirable. As for other units contained

in this hydroxyl-group content resin, vinyl ester unit; alkyl (meta) acrylate units, such as olefin units, such as ethylene and a propylene, and vinyl acetate, etc. are mentioned. Moreover, these hydroxyl-group content resin should have the molecular weight which is sufficient for forming a film at least.

[0028] Suitable hydroxyl-group content resin consists of a copolymer containing % of an ethylene unit, 10 thru/or 40-mol 40 thru/or % of a 88-mol vinyl alcohol unit, and the ester content vinyl unit not more than 50 mol %. By using such a hydroxyl-group content polymer as a blend object or a layered product, the gas barrier nature of a drawing Plastic solid can be raised, and the advantage of moreover not checking biodegradability on parenchyma is attained.

[0029] According to the application, the reinforcing agent of various coloring agents, a bulking agent, an inorganic system, or an organic system, lubricant, a plasticizer, a leveling agent, a surfactant, a thickener, an adhesiveness-reducing agent, a stabilizer, an anti-oxidant, an ultraviolet ray absorbent, a rusr-proofer, etc. can be blended with the drawing Plastic solid of this invention according to a well-known formula.

[0030] (A drawing Plastic solid and its process) The drawing Plastic solid of this invention is manufactured by performing biaxial stretching which prepared negative inclination in the drawing rate of making the drawing rate of a telophase small greatly [object / of the resin which makes aliphatic series polyester a subject / preforming / rate / early / drawing].

[0031] Manufacture of a preforming object (preforming) can be manufactured in itself by a well-known extrusion method and the well-known injection-molding method, and compression forming. For example, the light-gage sheet of an oriented film and a film, and the sheet pressure forming to a cup thru/or for plug assist forming are fabricated by extruding and carrying out melting resin through T-die. Moreover, pipe-like preforming for container shaping can also be fabricated by extruding and carrying out melting resin through a ring die. Furthermore, preforming for solid containers, such as a bottle, is fabricated by injecting melting resin by the screw or the plunger in the metal mold which consists of cavity metal mold and core metal mold. Moreover, preforming for stereos, such as a bottle, is obtained compressing the parison of melting resin with cavity metal mold and core metal mold.

[0032] In order to manufacture the preforming object which consists of the layered product of aliphatic series polyester and other resin, for example, hydroxyl-group content resin, a multilayer preforming object is manufactured by using a well-known laminating technique in itself, for example, co-extruding using a multilayer die using the extruder corresponding to the class of resin, when it is an extrusion method. Moreover, in injection molding, multilayer preforming can be formed in itself by the well-known simultaneous co-injecting method and the well-known serial co-injecting method. Furthermore, compression forming can also manufacture multilayer preforming by forming multilayer melting resin parison by co-extrusion etc.

[0033] Drawing shaping of a preforming object is performed in the drawing temperature of aliphatic series polyester on the conditions from which the approach which the drawing rate mentioned above is taken, and the orientation degree of crystallinity (Do) of the acquired Plastic solid becomes 0.15 or more.

[0034] Although drawing temperature is different with the class of aliphatic series polyester, generally, Tg thru/or Tg+60 degree C temperature are suitable on the basis of the glass transition point (Tg) of aliphatic series polyester, for example, when it is polylactic acid, the temperature which is Tg+10 degree C thru/or Tg+20 degree C is suitable.

[0035] Although biaxial-stretching shaping which prepared negative inclination in the drawing rate which made the drawing rate of a telophase small greatly [rate / early / drawing] is performed in this invention, it is desirable that the ratio (V1/V2) of the drawing rate (V1) of the 1st step and the drawing rate (V2) of the last stage is generally in the range of 3 thru/or 70, when canceling thru/or reducing a strong anisotropy. That is, since the productivity of drawing shaping will worsen if there is an inclination it to become difficult to improve a strength property so that said formula (1) may be satisfied, if the ratio of V1/V2 is less than the above-mentioned range, and this ratio exceeds the above-mentioned range on the other hand, it is not desirable.

[0036] Although especially the drawing rate in the 1st step is not limited, it is desirable that it is

generally in the range of 1 m/sec thru/or 50 m/sec. Change of a drawing rate can also be gradually changed over two steps or multistage [beyond it], and can also be changed continuously. Of course, inclination must be prepared in a drawing rate so that a drawing rate may decrease in monotone towards a tail end from the early stages of a drawing in any [these] case. A mechanical drawing can perform the change of a drawing rate by changing blow ** by expansion drawing by changing the passing speed of a drawing rod or a grasping chuck again.
[0037] The draw magnification of the direction of a machine (container shaft orientations) is [the draw magnification of 1.4 thru/or 4 times, and the crossing direction (container hoop direction)] 1.4 thru/or 4 times, and area draw magnification seems to become 2 thru/or 16 times suitably generally, as the orientation degree of crystallinity (Do) as which draw magnification is defined by said formula (2) becomes 0.15 or more.
[0038] In drawing shaping of this invention, the reason a strong anisotropy is canceled thru/or reduced has still come to be solved by preparing negative inclination in a drawing rate. However, on such drawing conditions, possibility that relaxation of distortion by drawing and a kind of heat setting have happened cannot be denied.
[0039] Although the anisotropy of a mechanical strength is canceled and the aliphatic series polyester drawing Plastic solid by this invention is excellent also in the various properties as a container, it has the inclination for it to be a little inferior in gas barrier nature as compared with aromatic polyester. In order to improve this, it is desirable to form the hard carbon film in one [at least] front face of a drawing Plastic solid with chemical vapor deposition (CVD).
[0040] The hard carbon film is a calling [the DLC (diamond like carbon) film i carbon film, or the hydrogenation amorphous carbon film (a-C:H)]-generally thing, and it consists of the amorphous carbon film which made SP3 association the subject. This carbon film is excellent in the sorption depressor effect **** gas barrier property of low-molecular organic compounds, such as a flavor component. As for the thickness of a carbon film, it is desirable that it is in the range of 0.05-5 micrometers from a standpoint with improvement in these properties, adhesion with plastics, endurance, transparency, etc.
[0041] chemical vapor deposition (CVD) with formation of the hard carbon film well-known in itself -- especially plasma CVD can perform. Plasma CVD performs thin film growth using the gas plasma, and fundamentally, make the gas which contains material gas under reduced pressure discharge with the electric energy by high electric field, it is made to decompose, and it consists of the process which makes the matter to generate deposit on a substrate through the chemical reaction the inside of a gaseous phase, or on a substrate. The plasma state is realized as boil glow discharge, and the approach of using direct-current glow discharge with the method of this glow discharge, the method of using RF glow discharge, the method of using microwave discharge, etc. are learned.
[0042] Since plasma CVD uses direct decomposition of the gas molecule by ** high-speed electron, it is in the thermal non-equilibrium which can dissociate the big material gas of generation energy easily and from which ** electron temperature and gas molecule temperature differ, has the advantage that the comparatively uniform amorphous film can be formed even if ** substrate temperature whose low-temperature process becomes possible is low, and can apply it also to an aliphatic series polyester drawing Plastic solid easily.
[0043] As material gas for film formation, the aliphatic hydrocarbon of a gas and ******, aromatic hydrocarbon, oxygenated hydrocarbons, and nitrogen-containing hydrocarbons are used in ordinary temperature. Also in this, six or more benzene, toluene, O-xylene, meta xylene, p-KISHIRE, a cyclohexane, etc. have a desirable carbon number. These raw materials can also be used independently, and may be used as two or more sorts of mixed gas, and these gas may be further diluted and used for them with rare gas like an argon or helium.
[0044] It is filled up with an aliphatic series polyester drawing Plastic solid in a reaction container at formation of the hard carbon film, and the inside of a reaction container is made reduced pressure. Generally the degree of vacuum at this time has the desirable range of 10-2 - 10-5torr. Subsequently, said material gas is supplied in a reaction container, glow discharge is started, and film formation is

performed. As for the pressure in a reaction container, it is desirable that it is in the range of 0.5 - 0.001torr. In order to raise the adhesion of a carbon film and a Plastic solid further, it precedes forming a carbon film, and by inorganic gas, such as an argon and oxygen, plasma treatment can be performed and a Plastic solid front face can also be activated.

[0045] (Application) The drawing Plastic solid of this invention is still still more useful as the structures, such as a pipe and a case, as containers for a negotiation, such as a container, a tank, and a cage, as various plastics containers, for example, a bottle, a cup, a tube, a plastics can, a pouch, a cap, and wrapping, such as a film and a tray.

[0046]

[Example] Next, this invention is explained with a concrete example. In addition, this invention is not limited to the following examples.

[0047] (Shaping)

Bottle shaping: Weight average molecular weight used the polylactic acid of 180000. Preforming with an aperture [phi] of 28mm was injection molded under 190-200-degree-C condition using the injection molding machine. The die temperature of 15 degrees C. Next, round 500ml ****** blow bottle was created for preforming after reheating at 65-75 degrees C using the metal mold blow molding machine at the infrared heater. In this case, it considered as the constant-pressure blow molding which makes blow ** compression pneumatic pressure 30 kg/cm2. Moreover, after it made compressed-air entrainment opening and an exhaust port put side by side and early compression pneumatic pressure considered as 30 kg/cm2, the exhaust air bulb was opened for a time, blow ** was gradually decreased in blow time amount, and the metal mold blow which decompressed final blow ** to 0.5 kg/cm2 was performed.

[0048] Cup shaping: Said polylactic acid was used. Using the extruder, C1-C4 of the screw section were made into 190-200 degrees C, T-die temperature was made into 190 degrees C, and the sheet of 400mm width of face and 2mm thickness was created. While extending this sheet to the lengthwise direction in the cone mold plug assist after reheating at 70 degrees C using the thermostat form making machine, the cylindrical cup was fabricated by the compressed air. (Aperture 80mmphi, diameter-of-bottom 50mmphi, height of 90mm) . The die temperature of 15 degrees C. In this case, shaping which made the pressure of the compressed air of an entrainment the constant pressure of 10 kg/cm2, and shaping to which the pressure of the entrainment compressed air was changed from the initial pneumatic pressure of 10kg/cm2 to 0.5kg/cm2 were performed.

[0049] Drawing sheet forming: Said polylactic acid was used. The 11mmx11mm size plate of 2mm thickness was injection molded under 190-200-degree-C condition using the injection molding machine. The die temperature of 15 degrees C. next, biaxial-stretching equipment -- using -- drawing rate 10 m/min after reheating an injection-molding plate at 70 degrees C -- 2x2 times, 2.5x2.5 times, and 3x3 times -- simultaneous biaxial stretching was carried out. Moreover, draw magnification was made into 3x3 times at regularity, and simultaneous biaxial stretching to which the drawing rate was changed with 50 mm/min, 500 mm/min, and 1000 mm/min was performed. Similarly, draw magnification was made into 3x3 times, initial drawing rates are 1000 mm/min and biaxial stretching which decelerated 500 mm/min, 50 mm/min, and a drawing rate gradually in biaxial-stretching time amount was performed.

[0050] (Assessment)

Drawing stress of a biaxial-stretching sheet: The drawing stress at the time of biaxial stretching was measured using Oriental energy machine company make and biaxial-stretching equipment. In this case, although drawing shafts were two shafts, the drawing stress of each drawing shaft showed this pattern. For this reason, the drawing stress of 1 shaft orientations was shown.

Mechanical strength: The biaxial-stretching sheet was used. The ASTMD-1822 mold dumbbell was started, respectively in the direction centering on the direction centering on drawing shaft orientations (X, Y), and the direction of a vertical angle (the direction of 45 degree) which drawing 2 shaft orientations make, and the tensile-stress-skew curve was obtained with the hauling testing machine made from ORIENTEC.

Compressive strength: The metal mold blow bottle and the thermostat form shaping cup were used. The jig of 10mmphi was used for the bottle and the drum section (longitudinal direction) of a cup, and the

compressive-strain trial of the 10% of the amounts of strains was performed. The bottle which generated the crack in the direction of a drum section at the time of strain deformation, and the cup were made into x, and the bottle which a crack does not generate at the time of deformation, and the cup were made into O.

[0051] 13C broad line NMR measurement: JEOL Shrine make After arranging and piling up the logging direction using a biaxial-stretching sheet, a metal mold blow bottle, and the intercept that arranged and started the direction from the thermostat foam cup to 4mm width of face using NMR equipment, the electrode holder made from die chlorofluocarbon was filled up. Then, 13C broad line NMR measurement was performed. Moreover, the view atomic nucleus was limited to the carbonyl carbon field. If the obtained NMR spectrum is only a non-orientation component, it shows the amorphism pattern shown in drawing 1 . If the orientation component exists, in addition to the amorphism pattern shown in drawing 2 , the orientation shaft of an orientation component as shown in drawing 3 and drawing 4 , and the include-angle dependence spectrum pattern which the direction of a static magnetic field of NMR makes are shown (an example, the drawing 3 -> perpendicularity, and drawing 4 -> parallel). For this reason, it can ask for the presentation molar fraction of an orientation crystal component by deducting the powder pattern shown in drawing 2 from 13C broad line NMR measurement spectrum of location survey. First, the light-gage amorphism sample which quenched the melting sample was created, finely, after decision, random restoration was carried out and 13C broad line NMR measurement was carried out at sample tubing made from die chlorofluocarbon (drawing 1). Next, the logging direction was arranged for the intercept cut down from the thermostat foam cup, and superposition and 13C broad line NMR measurement were performed in the biaxial-stretching sheet, the metal mold blow bottle, and the list. After reading each measured spectrum with an image scanner, X of a spectrum and a Y coordinate were obtained. Then, the powder pattern of a non-orientation component was deducted from 13C broad line NMR spectrum of the intercept of a thermostat foam cup in the biaxial-stretching sheet, the metal mold blow bottle, and the list by spreadsheet software (the Microsoft Corp. make, Excel (trademark)). Spectrum peak intensity before count was set to S. The amorphism component deducted by count was set to Sa. In this case, S-Sa=Sc serves as an orientation crystal component. For this reason, Do=(S-Sa)/S shows a formed part of an orientation crystal component here. 13C broad line NMR measurement shown here is general tools of analysis.

[0052] Simultaneous biaxial stretching of draw magnification 3x3 was performed using biaxial-stretching equipment after reheating the plate of [example 1] 2mm thickness at 70 degrees C. The initial drawing rate was made into 1000 mm/min, and the drawing rate was gradually reduced with 500 mm/min and 50 mm/min into simultaneous biaxial-stretching time amount. The orientation degree of crystallinity for which the drawing stress pattern at the time of the mechanical strength (yield point reinforcement) of drawing shaft orientations and its direction of a vertical angle (the direction of 45 degree) and biaxial stretching of this sample and the list were asked from 13C broad line NMR measurement was shown in a table 1 about the above-mentioned simultaneous biaxial-stretching sample.

[0053] Draw magnification performed simultaneous biaxial stretching of 3x3 using biaxial-stretching equipment after reheating the plate of [example 1 of comparison] 2mm thickness at 70 degrees C. The drawing rate was extended whenever [fixed-speed] at the rate of [each] 1000 mm/min, 500 mm/min, and 50 mm/min. The orientation degree of crystallinity for which the drawing stress pattern at the time of the mechanical strength (yield point reinforcement) of drawing shaft orientations and its direction of a vertical angle (the direction of 45 degree) and biaxial stretching of this sample and the list were asked from 13C broad line NMR was shown in a table 1 about the above-mentioned simultaneous biaxial-stretching sample.

[0054] Simultaneous biaxial stretching was performed using biaxial-stretching equipment after reheating the plate of [example 2 of comparison] 2mm thickness at 70 degrees C. The drawing rate was considered as whenever [fixed-speed / of 10 m/min], and draw magnification was changed with 2x2 times, 2.5x2.5 times, and 3x3 times. The orientation degree of crystallinity for which the drawing stress pattern at the time of the mechanical strength (yield point reinforcement) of drawing shaft orientations and its

direction of a vertical angle (the direction of 45 degree) and biaxial stretching of this sample and the list were asked from the 13 double width CNMR was shown in a table 2 about the above-mentioned simultaneous biaxial-stretching sample.

[0055] [Example 2] Said polylactic acid was used. The sheet of 400mm width of face which made C1-C4 of the screw section 190-200 degrees C, and made T-die temperature 190 degrees C, and 2mm thickness was created using the extruder. While extending this sheet to the lengthwise direction in the plug assist of a cone mold after reheating at 70 degrees C using the thermostat form making machine, it considered as 1 kg/cm2 low-voltage air from 2 the initial compression pneumatic pressure of 15kg/cm at the telophase, and the cylindrical cup was fabricated. (Aperture 80mmphi, diameter-of-bottom 50mmphi, height of 90mm) The die temperature of 15 degrees C. a cup drum section (longitudinal direction) -- 10mmphi plate jig -- using -- the 10% of the amounts of strains -- the compression set was carried out. The cup which a crack does not produce in a drum section at the time of compressive-strain deformation was made into O, and it considered as cup x which the crack produced at the drum section at the time of deformation. The result was shown in a table 3.

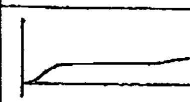
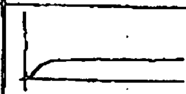
[0056] [Example 3 of a comparison] Said polylactic acid was used. The sheet of 2mm thickness was created using the extruder by 400mm width of face which made screw section temperature, and C1-C4 190-200 degrees C, and made T-die temperature 190 degrees C. While extending this sheet to the lengthwise direction in the cone mold plug assist after heating at 70 degrees C using the thermostat form making machine, it fabricated by the compressed air in the cylindrical cup. (Aperture 80mmphi, diameter-of-bottom 50mmphi, height of 90mm) The die temperature of 15 degrees C. In this case, the pressure of the compressed air of an entrainment was made into 15 kg/cm2. 10mmphi plate jig was used for the cup drum section (longitudinal direction), and compressive-strain deformation was carried out at the 10% of the amounts of strains. The cup which a crack does not produce in a drum section was made into O after strain deformation, and it considered as cup x which the crack produced in the drum section at the time of deformation. The result was shown in a table 3.

[0057] [Example 3] Said polylactic acid was used. Preforming of 28mmphi was injection molded under 190-200-degree-C condition using the injection molding machine. The die temperature of 15 degrees C. Round 500ml ** blow bottle was created for preforming with the metal mold blow molding machine after reheating at 70-75 degrees C using the infrared heater. After the blow pressure at the time of a blow made compressed-air entrainment opening and an exhaust port put side by side and made compression pneumatic pressure 30 kg/cm2 in early stages, it opened the exhaust air bulb for a time, and decompressed blow ** gradually in blow time amount. It decompressed to 0.5 kg/cm2 eventually, and the metal mold blow was carried out. Compressive-strain deformation of the drum section (longitudinal direction) of the above-mentioned shaping metal mold blow bottle was carried out to the 10% of the amounts of strains using 10mmphi plate jig. The bottle which a crack does not produce in a drum section was made into O after compressive-strain deformation, and it considered as bottle x which the crack produced in the drum section at the time of strain deformation. The result was shown in a table 3.

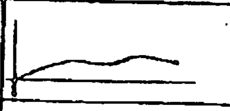
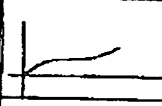
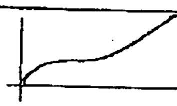
[0058] [Example 4 of a comparison] Said polylactic acid was used. Preforming of 28mm of diameters phi of a nozzle was injection molded under 190-200-degree-C condition using the injection molding machine. The die temperature of 15 degrees C. The round shape blow bottle of 500ml ** was created for preforming with the metal mold blow molding machine after reheating at 70-75 degrees C using the infrared heater. Constant-pressure blow molding which makes compression pneumatic pressure at the time of a blow 30 kg/cm2 was performed. the above-mentioned shaping metal mold blow bottle -- attaching -- a drum section (longitudinal direction) -- 10mmphi plate jig -- using -- the 10% of the amounts of strains -- compressive-strain deformation was carried out. The bottle which a crack does not produce in a drum section was made into O after compressive-strain deformation, and it considered as bottle x which the crack produced in the drum section at the time of strain deformation. The result was shown in a table 3.

[0059]

[A table 1]

	実施例1		比較例1					
延伸速度	勾配 初期 1000mm/min 中期 500mm/min 後期 50mm/min		定速 1000mm/min		定速 500mm/min		定速 50mm/min	
延伸倍率	3×3 倍同時二軸延伸		3×3 倍同時二軸延伸		3×3 倍同時二軸延伸		3×3 倍同時二軸延伸	
降伏点強度 Mpa	MD	45° (対角)	MD	45° (対角)	MD	45° (対角)	MD	45° (対角)
	96	91	95	97	94	96	113	116
機械的強度の異方性	MD>45°		MD<45°		MD<45°		MD<45°	
延伸応力パターン								
広幅 ^{13}C NMR 法による結晶化度	0.25		0.25		0.20		0.15	

[0060]
[A table 2]

	実施例1		比較例2					
延伸速度	勾配 初期 1000mm/min 中期 500mm/min 後期 50mm/min		定速 10m/min		定速 10m/min		定速 10mm/min	
延伸倍率	3×3 倍同時二軸延伸		2×2 倍同時二軸延伸		2.5×2.5 倍同時二軸延伸		3×3 倍同時二軸延伸	
降伏点強度 Mpa	MD	45° (対角)	MD	45° (対角)	MD	45° (対角)	MD	45° (対角)
	96	91	70	74	71	81	88	94
機械的強度の異方性	MD>45°		MD<45°		MD<45°		MD<45°	
延伸応力パターン								
広幅 ^{13}C NMR 法による結晶化度	0.25		0.05		0.20		0.25	

[0061]
[A table 3]

	カップ成形品		ボトル成形品	
	実施例2	比較例3	実施例3	比較例4
圧縮ひずみ 10%時 成型品の材料破壊	○	×	○	×

[0062] Next, preparation and measurement of a sample were shown in the example and the example of a comparison about the aliphatic series polyester drawing moldability in which the hard carbon film was formed.
[0063] (Bottle shaping) Preforming with an aperture [phi] of 28mm was injection molded under 190 degrees C - 200 degree-C condition using the injection molding machine for polylactic acid. The die temperature of 15 degrees C. Next, the metal mold blow bottle of 300 micrometers of average wall thickness of 500ml ** was created for preforming after reheating at 65-75 degrees C using the metal mold blow molding machine at the infrared heater. In this case, after making compressed-air entrainment opening and an exhaust port put side by side and making early compression pneumatic pressure into 30 kg/cm2, it decompressed in blow time amount gradually. Metal mold blow molding which made final blow pressure 0.5 kg/cm2 was performed. Moreover, metal mold blow molding which made blow pressure the constant pressure of 30 kg/cm2 was performed.
[0064] (Sheet forming) The sheet of 200mm width of face which made C1 - C4 temperature of the screw section 190 degrees C - 200 degrees C, and made T-die temperature 190 degrees C for polylactic acid using the extruder, and 2mm thickness was fabricated. Then, 3x3 times as many biaxial stretching as this was performed using the tenter type biaxial-stretching machine reheated and converted into 65 degrees C - 75 degrees C using heating oven (average wall thickness: 200 micrometers). In this case, the early drawing rate was made into 1 m/min, and by the time it resulted in predetermined draw magnification, the drawing rate was gradually slowed down to 0.05 m/min. Moreover, fixed-speed drawing shaping which made the drawing rate 1 m/min was performed.
[0065] (Film production of a carbon film) ****** 0.1torr and the PE-CVD carbon film vacuum evaporationo of 13.56MHz of high-frequency power which made hexane argon mixed gas material gas for bottle internal pressure after vacuum reduced pressure with CVD vacuum evaporationo equipment using the electrode of a bottle configuration and the electrode installed in the interior of a bottle were performed (bottle). Membrane formation temperature of 25 degrees C.
(Drawing sheet) ****** 0.1torr and the PE-CVD carbon film vacuum evaporationo of 13.56MHz of high-frequency power which made hexane argon mixed gas material gas were performed using the plate electrode set up up and down in the vacuum chamber. Membrane formation temperature of 25 degrees C.
[0066] (Oxygen gas barrier property)
(Bottle) The prototype bottle was put in in the vacuum chamber, after carrying out vacuum reduced pressure, high grade nitrogen gas was made to flow and nitrogen inert gas replacement of the bottle bashful phase was carried out. Then, it sealed with the rubber stopper. It saved on the 30 degree-C-RH80% conditions of 20.9% of oxygen densities. After three weeks, the gas-tight syringe was used, the air in a bottle was extracted, GC analysis was carried out, and it converted into BO2.
(Drawing sheet) Using the gas radiographic examination machine made from Mocon, oxygen transmittance was measured under 40-degree-C condition, and it converted into the oxygen transmission coefficient.
[0067] (Mechanical strength)
(Bottle) The jig of 10mmphi was used for the bottle drum section (longitudinal direction) after vapor-depositing a metal mold blow bottle and a carbon thin film, and the compressive-strain trial of the 10%

of the amounts of strains was performed. The bottle which the crack generated in the direction of a drum section at the time of strain deformation was made into x, and the bottle which a crack does not produce at the time of deformation was made into O.
(Drawing sheet) The ASTM-1822 mold dumbbell was started, respectively in the direction centering on the direction centering on drawing shaft orientations (X, Y) and the direction (45 degrees) of a vertical angle which drawing 2 shaft makes using a biaxial-stretching sheet, and the tensile-stress-skew curve was obtained with the hauling testing machine made from ORIENTEC.
[0068] Preforming with an aperture [phi] of 28mm was injection molded under 190 degrees C - 200 degree-C condition using the injection molding machine for [example 4] polylactic acid. The die temperature of 15 degrees C. Next, the metal mold blow bottle of 300 micrometers of average wall thickness of 500ml ** was created for preforming after reheating at 65 degrees C - 75 degrees C using the metal mold blow molding machine at the infrared heater. In this case, after making compressed-air entrainment opening and an exhaust port put side by side and making early compression pneumatic pressure into 30 kg/cm2, it decompressed in blow time amount gradually. Metal mold blow molding which made final blow pressure 0.5 kg/cm2 was performed. Next, ****** 0.1torr and the PE-CVD carbon film vacuum evaporationo of 13.56MHz of high-frequency power which make hexane argon mixed gas material gas for bottle internal pressure after vacuum reduced pressure with CVD vacuum evaporationo equipment using the electrode of a bottle configuration and the electrode installed in the interior of a bottle were performed. Membrane formation temperature of 25 degrees C. BO2 which saved the bottle after vapor-depositing a carbon film at 20.9% of 40 degree-C-RH80% of oxygen densities, and obtained it was obtained. Furthermore, the jig of 10mmphi was used for the bottle drum section (longitudinal direction), and the compressive-strain trial of the 10% of the amounts of strains was performed. The bottle which the crack generated in the direction of a drum section at the time of strain deformation was made into x, and the bottle which a crack does not produce at the time of deformation was made into O. The obtained result was shown in a table 4.
[0069] Preforming with an aperture [phi] of 28mm was injection molded under 190 degrees C - 200 degree-C condition using the injection molding machine for [example 5 of comparison] polylactic acid. The die temperature of 15 degrees C. Next, the metal mold blow bottle of 300 micrometers of average wall thickness of 500ml ** was created for preforming after reheating at 65 degrees C - 75 degrees C using the metal mold blow molding machine at the infrared heater. In this case, after making compressed-air entrainment opening and an exhaust port put side by side and making early compression pneumatic pressure into 30 kg/cm2, it decompressed in blow time amount gradually. Metal mold blow molding which made final blow pressure 0.5 kg/cm2 was performed. BO2 of a bottle which saved the above-mentioned bottle at 20.9% of 30 degree-C-RH80% of oxygen densities, and obtained it after the nitrogen purge was obtained. Furthermore, the jig of 10mmphi was used for the bottle drum section (longitudinal direction), and the compressive-strain trial of the 10% of the amounts of strains was performed. The bottle which the crack generated in the direction of a drum section at the time of strain deformation was made into x, and the bottle which a crack does not produce at the time of deformation was made into O. The obtained result was shown in a table 4.
[0070] Preforming with an aperture [phi] of 28mm was injection molded under 190 degrees C - 200 degree-C condition using the injection molding machine for [example 6 of comparison] polylactic acid. The die temperature of 15 degrees C. Next, the metal mold blow bottle of 300 micrometers of average wall thickness of 500ml ** was created for preforming after reheating at 65 degrees C - 75 degrees C using the metal mold blow molding machine at the infrared heater. In this case, metal mold blow molding which made the compressed-air pressure the 1 constant pressure of 30 kg/cm2 was performed. Next, ****** 0.1torr and the PE-CVD carbon film vacuum evaporationo of 13.56MHz of high-frequency power which make hexane argon mixed gas material gas for bottle internal pressure after vacuum reduced pressure with CVD vacuum evaporationo equipment using the electrode of a bottle configuration and the electrode installed in the interior of a bottle were performed. Membrane formation temperature of 25 degrees C. BO2 of a bottle which saved the bottle after vapor-depositing a carbon film at 20.9% of 30 degree-C-RH80% of oxygen densities, and obtained it was obtained. Furthermore, the jig

of 10mmphi was used for the bottle drum section (longitudinal direction), and the compressive-strain trial of the 10% of the amounts of strains was performed. The bottle which the crack generated in the direction of a drum section at the time of strain deformation was made into x, and the bottle which a crack does not produce at the time of deformation was made into O. The obtained result was shown in a table 4.

[0071] The sheet of 200mm width of face which made C1 - C4 temperature of the screw section 190 degrees C - 200 degrees C, and made T-die temperature 190 degrees C for [example 5] polylactic acid using the extruder, and 2mm thickness was fabricated. Then, 3x3 times as many biaxial stretching as this was performed using the tenter type biaxial-stretching machine reheated and converted into 65 degrees C - 75 degrees C using heating oven (average wall thickness: 200 micrometers). In this case, the early drawing rate was made into 10 m/min, and by the time it resulted in predetermined draw magnification, the drawing rate was gradually slowed down to 0.05 m/min. Next, ****** 0.1torr and the PE-CVD carbon film vacuum evaporationo of 13.56MHz of high-frequency power which made hexane argon mixed gas material gas were performed using the plate electrode set up up and down in the vacuum chamber. Membrane formation temperature of 25 degrees C. Furthermore, using the gas radiographic examination machine made from Mocon, oxygen transmittance was measured under 40-degree-C condition, and it converted into the oxygen transmission coefficient. Furthermore, the ASTM-1822 mold dumbbell was started, respectively in the direction centering on the direction centering on drawing shaft orientations (X, Y), and the direction (45 degrees) of a vertical angle which drawing 2 shaft makes, and the tensile-stress-skew curve was obtained with the hauling testing machine made from ORIENTEC. The obtained result was shown in a table 5.

[0072] The sheet of 200mm width of face which made C1 - C4 temperature of the screw section 190 degrees C - 200 degrees C, and made T-die temperature 190 degrees C for [example 7 of comparison] polylactic acid using the extruder, and 2mm thickness was fabricated. Then, 3x3 times as many biaxial stretching as this was performed using the tenter type biaxial-stretching machine reheated and converted into 65 degrees C - 75 degrees C using heating oven (average wall thickness: 200 micrometers). In this case, the early drawing rate was made into 10 m/min, and the drawing rate was gradually slowed down to 0.05 m/min until it resulted in predetermined draw magnification. Using the above-mentioned drawing sheet, using the gas radiographic examination machine made from Mocon, oxygen ****** was measured under 40-degree-C condition, and it converted into the oxygen transmission coefficient. Furthermore, the ASTM-1822 mold dumbbell was started, respectively in the direction centering on the direction centering on drawing shaft orientations (X, Y), and the direction (45 degrees) of a vertical angle which drawing 2 shaft makes, and the tensile-stress-skew curve was obtained with the hauling testing machine made from ORIENTEC. The obtained result was shown in a table 5.

[0073] The sheet of 200mm width of face which made C1 - C4 temperature of the screw section 190 degrees C - 200 degrees C, and made T-die temperature 190 degrees C for [example 8 of comparison] polylactic acid using the injection molding machine, and 2mm thickness was fabricated. Then, 3x3 times as many biaxial stretching as this was performed using the tenter type biaxial-stretching machine reheated and converted into 65 degrees C - 75 degrees C using heating oven (average wall thickness: 200 micrometers).

In this case, the drawing rate was made into the fixed drawing rate of 10 m/min. Next, ****** 0.1torr and the PE-CVD carbon film vacuum evaporationo of 13.56MHz of high-frequency power which make hexane argon mixed gas material gas for bottle internal pressure after vacuum reduced pressure with CVD vacuum evaporationo equipment using the electrode of a bottle configuration and the electrode installed in the interior of a bottle were performed. Membrane formation temperature of 25 degrees C. the above-mentioned drawing sheet -- using -- the gas radiographic examination machine made from Mocon -- using -- the bottom of 40-degree-C condition, and an oxygen transmission coefficient -- measuring -- base -- it converted into the transmission coefficient. Furthermore, the ASTM-1822 mold dumbbell was started, respectively in the direction centering on the direction centering on drawing shaft orientations (X, Y), and the direction (45 degrees) of a vertical angle which drawing 2 shaft makes, and the tensile-stress-skew curve was obtained with the hauling testing machine made from ORIENTEC.

The obtained result was shown in a table 5.
[0074]
[A table 4]

	実施例 4	比較例 5	比較例 6
ボトル平均肉厚	300 μm	300 μm	300 μm
炭素蒸着膜厚	0.1 μm	-	0.1 μm
酸素バリア性 1)	0.101	0.81	0.101
圧縮ひずみ 10%時のボトル強度	○	×	×

1)：単位, cc/bottle/day

[0075]
[A table 5]

	実施例 5		比較例 7		比較例 8	
平均肉厚	200 μm		200 μm		200 μm	
炭素蒸着膜厚	0.1 μm		-		0.1 μm	
酸素バリア性 2)	0.64		32.05		0.64	
延伸速度	勾配 初期 1000mm/min 中期 500mm/min 後期 50mm/min		勾配 初期 1000mm/min 中期 500mm/min 後期 50mm/min		定速 1000mm/min	
延伸倍率	3×3		3×3		3×3	
降伏点強度	MD	45° (対角)	MD	45° (対角)	MD	45° (対角)
	96	91	96	91	95	97
機械的強度の異方性	MD>45°		MD>45°		MD<45°	

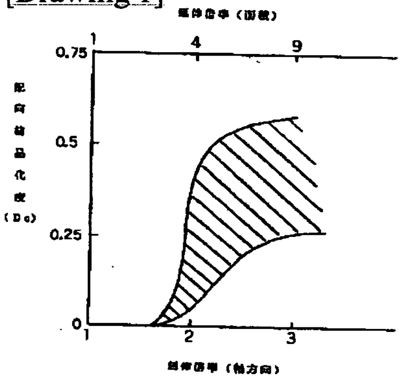
2): 単位, $cm^3(STP)/cm^2 \cdot sec \cdot cmHg$

[0076]
[Effect of the Invention] According to this invention, it is in the range in which the strength property of the drawing moldings of aliphatic series polyester is satisfied with the drawing rate which an early drawing rate is large and the drawing rate of a telophase makes small of said formula (1) by performing biaxial-stretching actuation which established negative inclination, and the anisotropy of a mechanical strength is canceled thru/or reduced and, moreover, an improvement of this anisotropy is attained in a field called 0.15 or more in the amount of preferred orientation (Do). The container which consists of a drawing Plastic solid of this invention has the advantage effectively prevented also to the crack by expansion contraction or deformation while it is excellent in buckling-proof nature or drop-proof impact nature. Furthermore, by making the hard carbon film form with chemical vapor deposition (CVD), permeability-proof can be raised to this aliphatic series polyester drawing Plastic solid, and, moreover, the sorption of a low-molecular organic component can also be controlled to it.

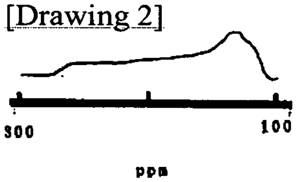
[Translation done.]

DRAWINGS

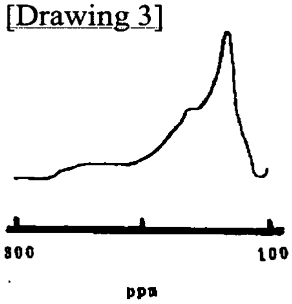
[Drawing 1]



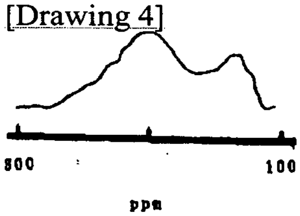
[Drawing 2]



[Drawing 3]



[Drawing 4]



[Translation done.]

(19)日本国特許庁（ＪＰ）　(12) 公開特許公報（Ａ）　(11)特許出願公開番号
特開2001－18290
（P2001－18290A）
(43)公開日　平成13年１月23日(2001.1.23)

(51)Int.Cl.⁷	識別記号	ＦＩ	テーマコート゛（参考）
Ｂ２９Ｃ　55/12		Ｂ２９Ｃ　55/12	３Ｅ０３３
Ｂ３２Ｂ　27/36		Ｂ３２Ｂ　27/36	４Ｆ１００
Ｂ６５Ｄ　1/09		Ｂ２９Ｃ　49/02	４Ｆ２０８
// Ｂ２９Ｃ　49/02		Ｂ６５Ｄ　1/00　　Ｃ	４Ｆ２１０
Ｂ２９Ｋ　67:00			

審査請求　未請求　請求項の数８　ＯＬ　（全 12 頁）　最終頁に続く

(21)出願番号　特願平11－193585
(22)出願日　平成11年７月７日(1999.7.7)

(71)出願人　000003768
東洋製罐株式会社
東京都千代田区内幸町１丁目３番１号
(72)発明者　伊藤　卓郎
神奈川県横須賀市長沢３－３－４
(72)発明者　山口　裕司
神奈川県川崎市中原区下小田６－７－27
(72)発明者　渡辺　祐登
神奈川県川崎市多摩区寺尾台１－4921
(72)発明者　有田　恒夫
神奈川県茅ヶ崎市松林２－11－45
(74)代理人　100067183
弁理士　鈴木　郁男

最終頁に続く

(54)【発明の名称】　脂肪族ポリエステル延伸成形体及びその製法

(57)【要約】
【課題】　脂肪族ポリエステルから形成された二軸延伸成形体において、上記の機械強度の異方性が解消乃至低減された機械的強度特性の安定した脂肪族ポリエステル二軸延伸成形体及びガスバリア性を向上させた脂肪族ポリエステル二軸延伸成形体の製造方法を提供することにある。
【解決手段】　脂肪族ポリエステルを主体とする樹脂の予備成形体を二軸延伸成形することからなる脂肪族ポリエステル延伸成形体の製法において、予備成形体の二軸延伸を、初期の延伸速度が大きく且つ終期の延伸速度が小さくなるように延伸速度に負の勾配を設けて成形することを、又、硬質炭素膜を蒸着することによりガスバリア性をも向上させることを特徴とする延伸成形体の製法。

【特許請求の範囲】

【請求項１】　脂肪族ポリエステルを主体とする樹脂の予備成形体を二軸延伸成形することからなる脂肪族ポリエステル延伸成形体の製法において、予備成形体の二軸延伸を、初期の延伸速度が大きく且つ終期の延伸速度が小さくなるように延伸速度に負の勾配を設けて成形することを特徴とする延伸成形体の製法。

【請求項２】　形成される脂肪族ポリエステル延伸成形体の少なくとも一方の表面に化学蒸着法により硬質炭素膜を形成することを特徴とする延伸成形体の製法。

【請求項３】　脂肪族ポリエステルを主体とする樹脂から形成された延伸成形体であって、下記式（１）

$T_{45} \leqq Tx$　‥（１）

式中、Ｔｘは成形体の二軸延伸方向の引張降伏点強度（ＭＰａ）であり、T_{45}は成形体の延伸方向に対して４５°方向の引張降伏点強度（ＭＰａ）である、で表される強度特性を有することを特徴とする脂肪族ポリエステル延伸成形体。

【請求項４】　下記式（２）

$Do = (S - Sa) / S$　‥（２）

式中、Ｓは成形体試料を^{13}Ｃ広幅ＮＭＲで測定したときの化学シフト１００乃至３００ｐｐｍのピーク面積を表し、Ｓａは前記試料の非晶質粉末について上記と同様に測定したときのＮＭＲスペクトルのピーク面積を表す、で定義される配向結晶化度（Ｄｏ）が０．１５以上であることを特徴とする請求項３記載の延伸成形体。

【請求項５】　脂肪族ポリエステルがガラス転移点（Ｔｇ）が－６０℃以上の脂肪族ポリエステルであることを特徴とする請求項３または４に記載の延伸成形体。

【請求項６】　脂肪族ポリエステルがポリヒドロキシアルカノエートであることを特徴とする請求項３または４に記載の延伸成形体。

【請求項７】　脂肪族ポリエステル延伸成形体の少なくとも一方の表面に硬質炭素膜が形成されていることを特徴とする請求項３乃至６の何れかに記載の延伸成形体。

【請求項８】　請求項３乃至７の何れかに記載の延伸成形体からなることを特徴とする包装容器。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、機械的強度の異方性を改善した脂肪族ポリエステルの延伸成形体及びその製造方法に関するものである。

【０００２】

【従来の技術】近年、都市が排出する固形廃棄物は、その量が段々膨大となり、廃棄処理能力の限界に近づきつつある。この固形廃棄物の元凶の一つとして、プラスチックがいつも指摘されている。

【０００３】プラスチック廃棄物の理想的解決法として、自然環境で消滅する分解性プラスチックが注目されている。分解性プラスチックには、紫外線によってポリマーの分子鎖が切断される光分解性プラスチックと、バクテリヤや真菌類が体外に放出する酵素の作用で崩壊する生分解性プラスチックとがある。

【０００４】しかしながら、光分解性プラスチックの場合、土中埋没処理では効果が期待できなく、また分解生成物による環境汚染の恐れもあることから、生分解性プラスチックに大きな期待が寄せられている。

【０００５】生分解性プラスチックとしては、従来、脂肪族ポリエステル、例えばポリヒドロキシブチレート（ＰＨＡ）、３－ヒドロキシブチレート（３ＨＢ）と３－ヒドロキシバリレート（３ＨＶ）とのランダムコポリマー、ポリ（ε－カプロラクトン）（ＰＣＬ）、ポリブチレンサクシネート（ＰＢＳ）、ポリブチレンサクシネート・アジペート（ＰＢＡＳ）、ポリ乳酸（ＰＬＬＡ）等が知られている。

【０００６】

【発明が解決しようとする問題点】しかしながら、これらの脂肪族ポリエステルは、生分解性など環境との調和の点では優れているものの、成形性の点で未だ解決しなければならない問題点を有している。１例として、脂肪族ポリエステルは、樹脂の溶融物性が劣り、ダイレクトブロー、射出延伸成形、シートのサーモフォーム成形などの成形が困難であるという問題を有している。このため、無機フィラーの添加による溶融張力の向上（特開平５－２８９６２３）やジイソシアネートやジエポキシ化合物、酸無水物を用いた鎖長延伸による高分子量化（特開平７－２０５２７８）が提案されている。又、脂肪族ポリエステルは一般に延伸成形による加工にて材料強度を向上させることができる。

【０００７】

【発明が解決しようとする課題】脂肪族ポリエステルは、通常のプラスチックと同様に、延伸により降伏点強度、弾性率などの機械的強度が向上する。しかし、脂肪族ポリエステルを二軸延伸成形した場合、得られた延伸成形物は機械的強度の異方性が生じる。

【０００８】例えば、芳香族ポリエステル、ポリエチレンテレフタレート（ＰＥＴ）の二軸延伸成形体においては、延伸方向、即ち機械方向（ＭＤ）及び横断方向（ＴＤ）の降伏点強度と、ＭＤ、ＴＤから４５度方向の降伏点強度がほぼ等しい強度を示すのに、ポリ乳酸のような脂肪族ポリエステルは、延伸方向、即ち機械方向（ＭＤ）及び横断方向（ＴＤ）の降伏点強度が、ＭＤ及びＴＤ方向から４５度の方向の降伏点強度より低下している。

【０００９】このように脂肪族ポリエステルの二軸延伸成形体は機械的強度の異方性が生じており、特に本来強度が増加すべき延伸軸方向で強度が低くなるため、成形体の強度設計が難しいという問題を有している。例えば、ボトルやカップなどの立体成形容器では、延伸方向を容器軸方向と容器周方向にとるのが適している。この

場合、延伸軸のなす面の機械的強度を等方的に存することは座屈防止や落下衝撃による割れ防止、膨張、収縮や変形による割れを防止にも重要な要点となっている。ところが、軸方向や周方向の強度が延伸軸と４５度方向をなす方向においても機械的強度が異なるため、脂肪族ポリエステルの二軸延伸成形体の強度は所期の目的を達成していない。一方、容器の軸方向や周方向から４５度偏った方向に延伸操作を行うことは実際的でない。

【００１０】しかも、上記のように機械的強度の異方性を有する二軸延伸成形体では、比較例に示すとおり、圧縮変形に際し、しばしば割れを発生する傾向もあることが分かった。

【００１１】したがって、本発明の目的は、脂肪族ポリエステルから形成された二軸延伸成形体において、上記の機械強度の異方性が解消乃至低減された機械的強度特性の安定した脂肪族ポリエステル二軸延伸成形体及びその製造方法を提供することにある。

【００１２】

【課題を解決するための手段】本発明によれば、脂肪族ポリエステルを主体とする樹脂の予備成形体を二軸延伸成形することからなる脂肪族ポリエステル延伸成形体の製法において、予備成形体の二軸延伸を、初期の延伸速度を大きく且つ終期の延伸速度を小さくしたように延伸速度に負の勾配を設けた延伸成形を特徴とする延伸成形体の製法が提供される。本発明によればまた、脂肪族ポリエステルを主体とする樹脂から形成された延伸成形体であって、下記式（１）

$$T_{45} \leqq Tx \quad \cdot\cdot (1)$$

式中、Ｔｘは成形体の二軸延伸方向の引張降伏点強度（ＭＰａ）であり、T_{45}は成形体の延伸方向に対して４５°方向の引張降伏点強度（ＭＰａ）である、で表される強度特性を有することを特徴とする脂肪族ポリエステル延伸成形体が提供される。本発明による脂肪族ポリエステル延伸成形体は、下記式（２）

$$Do = (S - Sa) / S \quad \cdot\cdot (2)$$

式中、Ｓは成形体試料を^{13}Ｃ広幅ＮＭＲで測定したときの化学シフト１００乃至３００ｐｐｍのピーク面積を表し、Ｓａは前記試料の非晶質粉末について上記と同様に測定したときのＮＭＲスペクトルのピーク面積を表す、で定義される配向結晶化度（Ｄｏ）が０．１５以上であることが好ましい。また、本発明に用いる脂肪族ポリエステルは、ガラス転移点（Ｔｇ）が－６０℃以上の脂肪族ポリエステルであり、ポリヒドロキシアルカノエートを示す。本発明によれば、更に、上記延伸成形体からなることを特徴とする包装容器が提供される。本発明による延伸成形体には、器壁を通してのガス透過性を抑制し、且つ内容物中の香味成分の収着を防止する目的で、化学蒸着法により硬質炭素膜を形成することができる。

【００１３】

【発明の実施形態】［作用］本発明は、脂肪族ポリエステル予備成形体の二軸延伸を、初期の延伸速度を大きく且つ終期の延伸速度を小さくした延伸速度に負の勾配を設けた延伸成形にて、延伸成形体の強度の異方性を解消乃至低減させうるという新規知見に基づくものである。

【００１４】即ち、本発明において、初期の延伸速度を大きく且つ終期の延伸速度を小さくする延伸速度に負の勾配を設けた二軸延伸操作を行うことで、脂肪族ポリエステル延伸成形体の機械的強度の異方性を解消乃至低減させるのに重要である。例えば、延伸速度が一定の速度で延伸を行った場合、延伸速度が大きい場合、小さい場合のどちらの場合においても延伸方向の降伏点強度は４５度方向（対角方向）の降伏点強度に比して低下している。これに対し、初期の延伸速度を大きくし、且つ終期の延伸速度を小さくする延伸速度に負の勾配を設けた延伸成形を行うことにより、延伸方向の降伏点強度を対角方向の降伏点強度と等しいか、或いはそれよりも大きくすることができる。結果、延伸方向の強度が低下するという不利益を解消することが可能となった。

【００１５】本発明による脂肪族ポリエステル延伸成形体は、前記式（１）を満足する強度特性を示す。このため、本発明の延伸成形体からなる容器は、耐座屈性や耐落下衝撃性に優れていると共に、膨張収縮や変形による割れも有効に防止されているという利点を有する。

【００１６】本発明による延伸成形体は、前記式（２）で定義される配向結晶化度（Ｄｏ）が０．１５以上、特に０．２以上であることが、機械的特性、透明性、耐熱性の点で好ましい。

【００１７】通常、芳香族カルボン酸を主体とする二塩基酸とグリコールとから誘導された熱可塑性ポリエステルは、配向による結晶化度を密度法にて測定することができ、測定される密度と結晶化度との関係が下記式（３）で表される。結晶化度

$$X_c = (\rho_c / \rho) \times \{ (\rho - \rho_{am}) / (\rho_c - \rho_{am}) \} \times 100 \quad \cdot\cdot (3)$$

式中、ρはｎ－ヘプタン－四塩化炭素系密度勾配管（池田理化製）で、２０℃測定されるサンプルの密度、ρ_{am}は非晶密度（１．３３５ｇ／ｃｍ^3）、ρ_cは結晶密度（１．４５５ｇ／ｃｍ^3）。

【００１８】ところが、脂肪族ポリエステルの場合、特にポリ乳酸などは非晶試料も高度に配向した試料も密度は殆ど一定であり、密度法を用い配向結晶化度を求めることができない。

【００１９】本発明者は、脂肪族ポリエステルを^{13}Ｃ広幅ＮＭＲで測定したときの化学シフト１００乃至３００ｐｐｍ（カルボニル炭素領域）のピーク面積が、脂肪族ポリエステルの配向の程度と密接な関係があり、この

ピーク面積から配向度を測定できることを見出した。即ち、脂肪族ポリエステル延伸成形体について、ＮＭＲスペクトルの面積Ｓを求め、次いでこの試料の非晶質粉末について上記と同様に測定したときのＮＭＲスペクトルのピーク面積Ｓａを求め、前記式（２）から配向結晶化度（Ｄｏ）を算出する。このように求められた配向結晶化度（Ｄｏ）と延伸倍率との間には１：１の対応がある。

【００２０】図１は、脂肪族ポリエステルの各種延伸成形体について、延伸倍率（軸方向延伸倍率、面積延伸倍率）と得られた配向結晶化度（Ｄｏ）との関係を示している。図１によると、延伸倍率が増大するにつれ、配向結晶化度向度が増大していることが解る。

【００２１】本発明によれば、以上説明したとおり、脂肪族ポリエステルを初期の延伸速度を大きく且つ終期の延伸速度を小さくする延伸速度に負の勾配を設けた二軸延伸操作を行うことにより、延伸成形物の強度特性が前記式（1）を満足する範囲にあって機械的強度の異方性解消乃至低減され、しかもこの異方性の改善が配向結晶化度（Ｄｏ）が０．１５以上の領域で達成される点に着目されるべきである。

【００２２】（脂肪族ポリエステル樹脂）本発明において、脂肪族ポリエステル樹脂としては、ヒドロキシアルカノエート単位を主体とする生分解性脂肪族ポリエステル樹脂の任意のものが使用される。この脂肪族ポリエステル樹脂は、少なくともフィルムを形成し得る分子量を有するべきであり、一般にその数平均分子量は、１００００乃至３０００００、特に２００００乃至２０００００の範囲にあるのがよい。好適な脂肪族ポリエステル樹脂の例は、ポリヒドロキシアルカノエート、或いはこれらの共重合体である。

【００２３】ポリヒドロキシアルカノエートとしては、下記式

【化１】

$$-[-O-\underset{\displaystyle R}{\overset{|}{CH}}-(CH_2)_n-\overset{\displaystyle O}{\overset{\|}{C}}-]-$$

式中、Ｒは水素原子、または直鎖或いは分岐鎖のアルキル基であり、ｎはゼロを含む正の整数である、で表される反復単位、例えば、

乳酸［Ｒ＝CH_3　、ｎ＝０、ＬＬＡ］、
３－ヒドロキシブチレート［Ｒ＝CH_3　、ｎ＝１、３ＨＢ］、
３－ヒドロキシバリレート［Ｒ＝CH_2　CH_3　、ｎ＝１、３ＨＶ］、
３－ヒドロキシカプロエート［Ｒ＝$(CH_2)_2$　CH_3　、ｎ＝１、３ＨＣ］、
３－ヒドロキシヘプタノエート［Ｒ＝$(CH_2)_3$　CH_3　、ｎ＝１、３ＨＨ］、
３－ヒドロキシオクタノエート［Ｒ＝$(CH_2)_4$　CH_3　ｎ＝１、３ＨＯ］、
３－ヒドロキシノナノエート［Ｒ＝$(CH_2)_5$　CH_3　、ｎ＝１、３ＨＮ］、
３－ヒドロキシデカノエート［Ｒ＝$(CH_2)_6$　CH_3　、ｎ＝１、３ＨＤ］、
γ－ブチロラクトン［Ｒ＝Ｈ、ｎ＝２、ＢＬ］、
δ－バレロラクトン［Ｒ＝Ｈ、ｎ＝３、ＶＬ］、
ε－カプロラクトン［Ｒ＝Ｈ、ｎ＝４、ＣＬ］

等の１種或いは２種以上からなる重合体が挙げられる。

【００２４】このポリヒドロキシアルカノエートは、ポリ乳酸（ポリ乳酸としては、構成単位がＬ－乳酸のみからなるポリ（Ｌ－乳酸）、Ｄ－乳酸のみからなるポリ（Ｄ－乳酸）およびＬ－乳酸単位とＤ－乳酸種任意の割合で存在するポリ（ＤＬ－乳酸）を示す。）又、ポリεカプロラクトンのような単独重合体であってもよく、他のヒドロキシアルカリエートとの共重合体でもよい。また３－ヒドロキシブチレートと、他の３－ヒドロキシアルカノエート、特に３－ヒドロキシバリレートとを共重合させた共重合体であってもよい。

【００２５】本発明に用いる脂肪族ポリエステルは、ガラス転移点（Ｔｇ）が－６０℃以上、特に３０℃以上のものが好ましい。これらの脂肪族ポリエステルの内、工業的に量産され入手が容易であり、環境にも優しい脂肪族ポリエステルとして、ポリ乳酸が挙げられる。ポリ乳酸（ＰＬＬＡ）は、トウモロコシなどの穀物デンプンを原料とする樹脂であり、デンプンの乳酸発酵物、Ｌ－乳酸をモノマーとする重合体である。一般にそのダイマーであるラクタイドの開環重合法、及び、直接重縮合法により製造される。この重合体は、自然界に存在する微生物により、水と炭酸ガスにより分解され、完全リサイクルシステム型の樹脂として着目されている。また、そのガラス転移点（Ｔｇ）も約５８℃とＰＥＴのＴｇに近い

という利点を有している。

【0026】本発明の延伸成形体は、上記脂肪族ポリエステル、特にポリ乳酸を単独で使用することもできるし、他の脂肪族ポリエステル或いは他の樹脂とのブレンド物或いは他の樹脂との積層体としても用いることもできる。

【0027】更に、上記脂肪族ポリエステルとのブレンド物或いは積層体の形で使用可能な他の樹脂としては、バリアー樹脂、例えば酸素に対してバリアー性を示す水酸基含有熱可塑性樹脂、ナイロン樹脂、バリアー性ポリエステル樹脂、ハイニトリル樹脂や、水蒸気に対してバリアー性を示す環状オレフィン系共重合体等を挙げることができる。これらの内でも、生分解性の点では水酸基含有樹脂が好ましく、熱成形が可能である限り、任意の樹脂を用いることができる。この樹脂は、その分子鎖中に、水酸基を有する反復単位と、樹脂に熱成形性を付与する単位とを有している。水酸基含有反復単位はビニルアルコール単位、ヒドロキシアルキル（メタ）アクリレート単位であってよいが、生分解性の点ではビニルアルコール単位が好ましい。この水酸基含有樹脂中に含有される他の単位は、エチレン、プロピレン等のオレフィン単位、酢酸ビニル等のビニルエステル単位；アルキル（メタ）アクリレート単位等が挙げられる。又、これらの水酸基含有樹脂は、少なくともフィルムを形成するに足る分子量を有するべきである。

【0028】好適な水酸基含有樹脂は、１０乃至４０モル％のエチレン単位と、４０乃至８８モル％のビニルアルコール単位と、５０モル％以下のエステル含有ビニル単位とを含有する共重合体からなる。このような水酸基含有重合体をブレンド物或いは積層体として用いることで、延伸成形体のガスバリアー性を向上させることができ、しかも生分解性を実質上阻害しないという利点が達成される。

【0029】本発明の延伸成形体には、その用途に応じて、各種着色剤、充填剤、無機系或いは有機系の補強剤、滑剤、可塑剤、レベリング剤、界面活性剤、増粘剤、減粘剤、安定剤、抗酸化剤、紫外線吸収剤、防錆剤等を、公知の処方にしたがって配合することができる。

【0030】（延伸成形体及びその製法）本発明の延伸成形体は、脂肪族ポリエステルを主体とする樹脂の予備成形体を、初期の延伸速度を大きく且つ終期の延伸速度を小さくするという延伸速度に負の勾配を設けた二軸延伸を行うことにより製造される。

【0031】予備成形体（プリフォーム）の製造は、それ自体公知の押出成形法や射出成形法、圧縮成形法で製造することができる。例えば、溶融樹脂をＴ－ダイを通して押し出しすることにより、延伸フィルムの薄肉シート、及び、フィルムや、カップへの圧空成形乃至プラグアシスト成形用のシートが成形される。また、溶融樹脂をリングダイを通して押し出しすることにより、容器成形用のパイプ状プリフォームも成形することができる。更に、溶融樹脂を、スクリュー或いはプランジャーにより、キャビテイ金型とコア金型とからなる金型中に射出することで、ボトルなどの立体容器用のプリフォームが成形される。また、溶融樹脂のパリソンをキャビテイ金型とコア金型で圧縮することでもボトルなどの立体用プリフォームが得られる。

【0032】脂肪族ポリエステルと他の樹脂、例えば水酸基含有樹脂との積層体から成る予備成形体を製造するには、それ自体公知の積層技術が使用され、例えば押出成形法の場合、樹脂の種類に対応する押出機を用い、多層ダイを用いて共押出することにより、多層の予備成形体を製造する。また、射出成形では、それ自体公知の同時共射出法や逐次共射出法により、多層プリフォームを形成することができる。更に、圧縮成形法でも、共押出などにより多層の溶融樹脂パリソンを形成することで、多層プリフォームを製造することができる。

【0033】予備成形体の延伸成形は、脂肪族ポリエステルの延伸温度において、延伸速度が前述した方法をとり、且つ得られた成形体の配向結晶化度（Ｄｏ）が０．１５以上となる条件で行う。

【0034】延伸温度は、脂肪族ポリエステルの種類によっても相違するが、一般的にいって、脂肪族ポリエステルのガラス転移点（Ｔｇ）を基準とし、Ｔｇ乃至Ｔｇ＋６０℃の温度が適当であり、例えばポリ乳酸の場合、Ｔｇ＋１０℃乃至Ｔｇ＋２０℃の温度が適当である。

【0035】本発明では、初期の延伸速度を大きく且つ終期の延伸速度を小さくした延伸速度に負の勾配を設けた二軸延伸成形を行うが、第１段の延伸速度（V_1）と最終段の延伸速度（V_2）の比（V_1/V_2）が、一般に３乃至７０の範囲にあることが、強度の異方性を解消乃至低減させる上で好ましい。即ち、V_1/V_2の比が上記範囲を下回ると、前記式（１）を満足するように強度特性を改善することが困難となる傾向があり、一方、この比が上記範囲を上回ると延伸成形の生産性が悪くなるので好ましくない。

【0036】第１段目における延伸速度は、特に限定されないが、一般に１ｍ／ｓｅｃ乃至５０ｍ／ｓｅｃの範囲にあるのが望ましい。延伸速度の変化は、二段或いはそれ以上の多段にわたって段階的に変化させることもできるし、また連続的に変化させることもできる。勿論、これら何れの場合にも、延伸初期から終段に向けて延伸速度が単調に減少するよう延伸速度に勾配を設けなければならない。延伸速度の切り替えは、機械的延伸では延伸棒や把持チャックの移動速度を変化させることにより、また膨張延伸ではブロー圧を変化させることにより行うことができる。

【0037】延伸倍率は、前記式（２）で定義される配向結晶化度（Ｄｏ）が０．１５以上となるようなものであり、一般的にいって、機械方向（容器軸方向）の延伸

倍率が１．４乃至４倍、横断方向（容器周方向）の延伸倍率が１．４乃至４倍で、好適には面積延伸倍率が２乃至１６倍となるようなものである。

【００３８】本発明の延伸成形において、延伸速度に負の勾配を設けることにより、強度の異方性が解消乃至低減される理由は未だ解明されるには至っていない。しかしながら、このような延伸条件では、延伸による歪みの緩和と一種の熱固定とが起こっている可能性が否定できない。

【００３９】本発明による脂肪族ポリエステル延伸成形体は、機械的強度の異方性が解消されており、容器としての種々の特性にも優れているが、芳香族ポリエステルに比してガスバリアー性においてやや劣る傾向がある。これを改善するために、延伸成形体の少なくとも一方の表面に硬質炭素膜を化学蒸着法（ＣＶＤ）で形成することが好ましい。

【００４０】硬質炭素膜とは、一般にＤＬＣ（ｄｉａｍｏｎｄ ｌｉｋｅ ｃａｒｂｏｎ）膜、ｉカーボン膜または水素化アモルファスカーボン膜（ａ－Ｃ：Ｈ）と呼ばれるのものであり、ＳＰ^3 結合を主体にしたアモルファスな炭素膜から成っている。この炭素膜は、香味成分などの低分子有機化合物の収着抑制効果およびガスバリア性に優れている。炭素膜の厚みは、これらの特性の向上と、プラスチックとの密着性、耐久性および透明性等との見地から、０．０５～５μmの範囲にあることが好ましい。

【００４１】硬質炭素膜の形成は、それ自体公知の化学蒸着法（ＣＶＤ）、特にプラズマＣＶＤにより行うことができる。プラズマＣＶＤとは、気体プラズマを利用して薄膜成長を行うものであり、基本的には、減圧下において原料ガスを含むガスを高電界による電気的エネルギーで放電させ、分解させ、生成する物質を気相中或いは基板上での化学反応を経て、基板上に堆積させるプロセスから成る。プラズマ状態は、グロー放電をによって実現されるものであり、このグロー放電の方式によって、直流グロー放電を利用する方法、高周波グロー放電を利用する方法、マイクロ波放電を利用する方法などが知られている。

【００４２】プラズマＣＶＤは、①高速電子によるガス分子の直接分解を利用しているため、生成エネルギーの大きな原料ガスを容易に解離できる、②電子温度とガス分子温度が異なる熱的非平衡状態にあり、低温プロセスが可能となる、③基板温度が低くても比較的均一なアモルファス膜を形成できる、という利点を有するものであり、脂肪族ポリエステル延伸成形体にも容易に適用できるものである。

【００４３】膜形成用の原料ガスとしては、常温で気体または液体の脂肪族炭化水素類，芳香族炭化水素類，含酸素炭化水素類、含窒素炭化水素類などが使用される。この中でも、炭素数が6以上のベンゼン、トルエン、ｏ－キシレン、ｍ－キシレン、ｐ－キシレ、シクロヘキサン等が望ましい。これらの原料は、単独で用いることもできるし、２種以上の混合ガスとして使用してもよく、さらに、これらのガスをアルゴンやヘリウムの様な希ガスで希釈して用いてもよい。

【００４４】硬質炭素膜の形成には、反応容器内に脂肪族ポリエステル延伸成形体を充填し、反応容器内を減圧にする。このときの真空度は一般的に１０$^{-2}$～１０$^{-5}$ ｔｏｒｒの範囲が望ましい。次いで、反応容器内に前記原料ガスを供給し、グロー放電を開始して、膜形成を行う。反応容器内の圧力は０．５～０．００１ｔｏｒｒの範囲にあることが好ましい。炭素膜と成形体との密着性をさらに向上させるために、炭素膜を形成するに先だって、アルゴンや酸素などの無機ガスによってプラズマ処理を行い、成形体表面を活性化させることもできる。

【００４５】（用途）本発明の延伸成形体は、各種プラスチック包装容器、例えばボトル、カップ、チューブ、プラスチック缶、パウチ、キャップ等として、またフィルム、トレイ等の包装材料として、更にコンテナー、タンク、篭等の流通用容器として、更にパイプ、ケース等の構造物として有用である。

【００４６】

【実施例】次に、具体的な実施例をもって本発明を説明する。尚、本発明は以下の実施例に限定されるものではない。

【００４７】（成形）

ボトル成形：重量平均分子量が１８００００のポリ乳酸を用いた。射出成形機を用い、１９０～２００℃条件下、口径２８mmφのプリフォームを射出成形した。金型温度１５℃。次に、プリフォームを赤外線ヒーターにて６５～７５℃に再加熱後、金型ブロー成形機を用い、丸形の５００ｍｌ容金型ブローボトルを作成した。この場合、ブロー圧を圧縮空気圧３０Ｋｇ／ｃｍ^2 とする定圧ブロー成形とした。又、圧縮空気吹き込み口と排気口を併設させ、初期の圧縮空気圧が３０Ｋｇ／ｃｍ^2 とした後、排気バルブを暫時開放し、ブロー時間内に段階的にブロー圧を減少させ、最終的なブロー圧を０．５Ｋｇ／ｃｍ^2 まで減圧した金型ブローを行った。

【００４８】カップ成形：前記ポリ乳酸を用いた。押し出し機を用い、スクリュー部のＣ１～Ｃ４を１９０～２００℃、Ｔダイ温度を１９０℃とし、４００mm幅、２mm厚のシートを作成した。このシートをサーモフォーム成形機を用い、７０℃に再加熱後、円錐型プラグアシストにて縦方向に延伸すると同時に圧縮空気で円柱状カップを成形した。（口径８０mmφ，底径５０mmφ，高さ９０mm）。金型温度１５℃。この場合、吹き込みの圧縮空気の圧力を１０Ｋｇ／ｃｍ^2 の定圧とした成形と、吹き込み圧縮空気の圧力を初期空気圧１０ｋｇ／ｃｍ^2 から０．５ｋｇ／ｃｍ^2 まで変化させた成形を行っ

た。

【００４９】延伸シート成形：前記ポリ乳酸を用いた。射出成形機を用い、１９０～２００℃条件下、２mm厚の１１mm×１１mmサイズ平板を射出成形した。金型温度１５℃。次に、二軸延伸装置を用い射出成形平板を７０℃に再加熱後、延伸速度１０m／minにて、２×２倍、２．５×２．５倍、３×３倍の同時二軸延伸した。又、延伸倍率を３×３倍と一定にし、延伸速度を５０mm／min、５００mm／min、１０００mm／minと変化させた同時二軸延伸を行った。同様に、延伸倍率を３×３倍とし、初期延伸速度が１０００mm／minであり、二軸延伸時間内に、段階的に５００mm／min、５０mm／minと延伸速度を減速させた二軸延伸を行った。

【００５０】（評価）

二軸延伸シートの延伸応力：東洋精機社製、二軸延伸装置を用い、二軸延伸時の延伸応力を測定した。この場合、延伸軸は二軸であるが、それぞれの延伸軸の延伸応力は同パターンを示した。このため、一軸方向の延伸応力を示した。

機械的強度：二軸延伸シートを用いた。延伸軸方向（X，Y）を軸とする方向、及び、延伸二軸方向のなす対角方向（４５°方向）を軸とする方向にそれぞれＡＳＴＭＤ－１８２２型ダンベルを切り出し、ＯＲＩＥＮＴＥＣ社製引っ張り試験機にて引っ張り応力－ひずみ曲線を得た。

圧縮強度：金型ブローボトルとサーモフォーム成形カップを用いた。ボトル、及び、カップの胴部（横方向）に１０mmφのジグを用い、ひずみ量１０％の圧縮ひずみ試験を行った。ひずみ変形時に胴部方向に割れを生成したボトル、及び、カップを×とし、変形時に割れが生成しないボトル、及び、カップを○とした。

【００５１】^{13}Ｃ広幅ＮＭＲ測定：ＪＥＯＬ　社製ＮＭＲ装置を用い、二軸延伸シート、金型ブローボトル、及び、サーモフォームカップから４mm幅に方向をそろえて切り出した切片を用い、切り出し方向をそろえて重ね合わせた後、ダイフロン製ホルダーに充填した。その後、^{13}Ｃ広幅ＮＭＲ測定を行った。又、着目原子核をカルボニル炭素領域に限定した。得られたＮＭＲスペクトルは、無配向成分のみであれば、図１に示す非晶パターンを示す。もし、配向成分が存在していれば、図２に示す非晶パターンに加え、図３，図４に示すような配向成分の配向軸とＮＭＲの静磁場方向のなす角度依存スペクトルパターンを示す（例、図３→垂直，図４→平行）。このため、実測の^{13}Ｃ広幅ＮＭＲ測定スペクトルから図２に示すパウダーパターンを差し引くことで、配向結晶成分の組成分率を求めることができる。はじめに、溶融試料を急冷した薄肉非晶試料を作成し、細かく裁断後、ダイフロン製試料管にランダム充填し、^{13}Ｃ広幅ＮＭＲ測定した（図１）。次に、二軸延伸シート、金型ブローボトル、並びに、サーモフォームカップから切り出した切片を、切り出し方向をそろえて重ね合わせ、^{13}Ｃ広幅ＮＭＲ測定を行った。それぞれの実測スペクトルをイメージスキャナーで読みとった後、スペクトルのＸ，Ｙ座標を得た。その後、表計算ソフトウェア（マイクロソフト社製、Ｅｘｃｅｌ（登録商標））にて、二軸延伸シート、金型ブローボトル、並びに、サーモフォームカップの切片の^{13}Ｃ広幅ＮＭＲスペクトルから無配向成分のパウダーパターンを差し引いた。計算前のスペクトルピーク強度をＳとした。計算で差し引いた非晶成分をＳａとした。この場合、Ｓ－Ｓａ＝Ｓｃが配向結晶成分となる。このため、ここでは、Ｄｏ＝（Ｓ－Ｓａ）／Ｓが配向結晶成分の組成分を示す。ここで示した、^{13}Ｃ広幅ＮＭＲ測定は一般的な分析手法である。

【００５２】［実施例１］２mm厚の平板を７０℃に再加熱後、二軸延伸装置を用い延伸倍率３×３の同時二軸延伸を行った。初期延伸速度を１０００mm／minとし、同時二軸延伸時間内に、段階的に延伸速度を５００mm／min、５０mm／minと低下させた。上記同時二軸延伸試料につき、延伸軸方向とその対角方向（４５°方向）の機械的強度（降伏点強度）、同試料の二軸延伸時の延伸応力パターン、並びに、^{13}Ｃ広幅ＮＭＲ測定から求めた配向結晶化度を表１に示した。

【００５３】［比較例１］２mm厚の平板を７０℃に再加熱後、二軸延伸装置を用い延伸倍率が３×３の同時二軸延伸を行った。延伸速度を１０００mm／min、５００mm／min、５０mm／minのそれぞれの速度にて定速度延伸した。上記同時二軸延伸試料につき、延伸軸方向とその対角方向（４５°方向）の機械的強度（降伏点強度）、同試料の二軸延伸時の延伸応力パターン、並びに、^{13}Ｃ広幅ＮＭＲから求めた配向結晶化度を表１に示した。

【００５４】［比較例２］２mm厚の平板を７０℃に再加熱後、二軸延伸装置を用い同時二軸延伸を行った。延伸速度を１０m／minの定速度とし、延伸倍率を２×２倍、２．５×２．５倍、３×３倍と変化させた。上記同時二軸延伸試料につき、延伸軸方向とその対角方向（４５°方向）の機械的強度（降伏点強度）、同試料の二軸延伸時の延伸応力パターン、並びに、^{13}広幅ＣＮＭＲから求めた配向結晶化度を表２に示した。

【００５５】［実施例２］前記ポリ乳酸を用いた。押し出し機を用い、スクリュー部のＣ１～Ｃ４を１９０～２００℃、Ｔダイ温度を１９０℃とした、４００mm幅、２mm厚のシートを作成した。このシートをサーモフォーム成形機を用い、７０℃に再加熱後、円錐型のプラグアシストにて縦方向に延伸すると同時に初期圧縮空気圧１５Ｋｇ／ｃｍ^{2}から終期に１Ｋｇ／ｃｍ^{2}低圧空気とし円柱状カップを成形した。（口径８０mmφ，底径５０mmφ，高さ９０mm）金型温度１５℃。カップ胴部

（横方向）に１０ｍｍφ平板ジグを用い、ヒズミ量１０％の圧縮変形させた。圧縮ひずみ変形時に、胴部に割れが生じないカップを○とし、変形時に胴部に割れが生じたカップ×とした。結果を表３に示した。

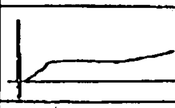
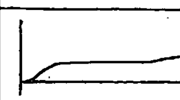
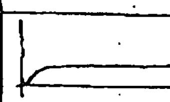
【００５６】［比較例３］前記ポリ乳酸を用いた。押し出し機を用い、スクリュー部温度、Ｃ１～Ｃ４を１９０～２００℃、Ｔダイ温度を１９０℃とした、４００ｍｍ幅で２ｍｍ厚のシートを作成した。このシートをサーモフォーム成形機を用い、７０℃に加熱後、円錐型プラグアシストにて縦方向に延伸すると同時に圧縮空気で円柱状カップに成形した。（口径８０ｍｍφ，底径５０ｍｍφ，高さ９０ｍｍ）金型温度１５℃。この場合、吹き込みの圧縮空気の圧力を１５Ｋｇ／ｃｍ^2 とした。カップ胴部（横方向）に１０ｍｍφ平板ジグを用い、ひずみ量１０％で圧縮ひずみ変形させた。ひずみ変形後、胴部に割れが生じないカップを○とし、変形時に胴部に割れが生じたカップ×とした。結果を表３に示した。

【００５７】［実施例３］前記ポリ乳酸を用いた。射出成形機を用い、１９０～２００℃条件下、２８ｍｍφのプリフォームを射出成形した。金型温度１５℃。プリフォームを赤外線ヒーターを用い７０～７５℃に再加熱後、金型ブロー成形機にて丸形の５００ｍｌ容ブローボトルを作成した。ブロー時のブロー圧力は、圧縮空気吹き込み口と排気口を併設させ、初期に圧縮空気圧を３０Ｋｇ／ｃｍ^2 とした後、排気バルブを暫時開放し、ブロー時間内にブロー圧を段階的に減圧した。最終的に０．５Ｋｇ／ｃｍ^2 まで減圧し金型ブローをした。上記成形金型ブローボトルの胴部（横方向）を、１０ｍｍφ平板ジグを用い、ヒズミ量１０％まで圧縮ひずみ変形させた。圧縮ひずみ変形後、胴部に割れが生じないボトルを○とし、ひずみ変形時に胴部に割れが生じたボトル×とした。結果を表３に示した。

【００５８】［比較例４］前記ポリ乳酸を用いた。射出成形機を用い、１９０～２００℃条件下、ノズル径２８ｍｍφのプリフォームを射出成形した。金型温度１５℃。プリフォームを赤外線ヒーターを用い７０～７５℃に再加熱後、金型ブロー成形機で５００ｍｌ容の丸形ブローボトルを作成した。ブロー時の圧縮空気圧を３０Ｋｇ／ｃｍ^2 とする定圧ブロー成形を行った。上記成形金型ブローボトルにつき、胴部（横方向）を１０ｍｍφ平板ジグを用い、ヒズミ量１０％の圧縮ひずみ変形させた。圧縮ひずみ変形後、胴部に割れが生じないボトルを○とし、ひずみ変形時に胴部に割れが生じたボトル×とした。結果を表３に示した。

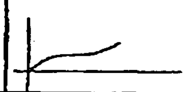
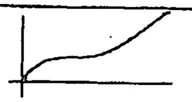
【００５９】

【表１】

	実施例1		比較例1					
延伸速度	勾配 初期 1000mm/min 中期 500mm/min 後期 50mm/min		定速 1000mm/min		定速 500mm/min		定速 50mm/min	
延伸倍率	3×3 倍同時二軸延伸		3×3 倍同時二軸延伸		3×3 倍同時二軸延伸		3×3 倍同時二軸延伸	
降伏点強度 Mpa	MD	45° (対角)	MD	45° (対角)	MD	45° (対角)	MD	45° (対角)
	96	91	95	97	94	96	113	116
機械的強度の異方性	MD>45°		MD<45°		MD<45°		MD<45°	
延伸応力パターン								
広幅^{13}C NMR法による結晶化度	0.25		0.25		0.20		0.15	

【００６０】

【表２】

	実施例1		比較例2					
延伸速度	勾配 初期 1000mm/min 中期 500mm/min 後期 50mm/min		定速 10m/min		定速 10m/min		定速 10mm/min	
延伸倍率	3×3 倍同時二軸延伸		2×2 倍同時二軸延伸		2.5×2.5 倍同時二軸延伸		3×3 倍同時二軸延伸	
降伏点強度 Mpa	MD	45° (対角)	MD	45° (対角)	MD	45° (対角)	MD	45° (対角)
	96	91	70	74	71	81	88	94
機械的強度の異方性	MD＞45°		MD＜45°		MD＜45°		MD＜45°	
延伸応力パターン								
広幅 ^{14}C NMR 法による結晶化度	0.25		0.05		0.26		0.25	

【００６１】

【表３】

	カップ成形品		ボトル成形品	
	実施例２	比較例３	実施例３	比較例４
圧縮ひずみ 10%時 成型品の材料強度	○	×	○	×

【００６２】次に硬質炭素膜を形成した脂肪族ポリエステル延伸成形性に関する実施例及び比較例において、試料の調製及び測定を示した。

【００６３】（ボトル成形）ポリ乳酸を射出成形機を用い、１９０℃～２００℃条件下、口径２８mmφのプリフォームを射出成形した。金型温度１５℃。次に、プリフォームを赤外線ヒーターにて６５～７５℃に再加熱後、金型ブロー成形機を用い、５００ml容の平均肉厚３００μmの金型ブローボトルを作成した。この場合、圧縮空気吹き込み口と排気口を併設させ、初期の圧縮空気圧を３０Kg／cm^2 とした後、段階的にブロー時間内に減圧した。最終的なブロー圧力を０．５Kg／cm^2 とした金型ブロー成形を行った。又、ブロー圧力を３０Kg／cm^2 の定圧とした金型ブロー成形を行った。

【００６４】（シート成形）ポリ乳酸を押し出し機を用い、スクリュー部のＣ１～Ｃ４温度を１９０℃～２００℃、Ｔダイ温度を１９０℃とした、２００mm幅、２mm厚のシートを成形した。その後、加熱オーブンを用い、６５℃～７５℃に再加熱し、改造したテンター式二軸延伸機を用い、３×３倍の二軸延伸を行った（平均肉厚：２００μm）。この場合、初期の延伸速度を１m／minとし、所定の延伸倍率に至るまでに延伸速度を０．０５m／minに段階的に減速した。又、延伸速度を１m／minとした定速延伸成形を行った。

【００６５】（炭素膜の製膜）（ボトル）ＣＶＤ蒸着装置にて、ボトル形状の電極とボトル内部に設置した電極を用い、ボトル内圧力を真空減圧後、ヘキサン・アルゴン混合ガスを原料ガスとした、成膜圧０．１torr、高周波電力１３．５６MHzのＰＥ－ＣＶＤ炭素膜蒸着を行った。成膜温度２５℃。

（延伸シート）真空チャンバー内上下に設定した平板電極を用い、ヘキサン・アルゴン混合ガスを原料ガスとした、成膜圧０．１torr、高周波電力１３．５６MHzのＰＥ－ＣＶＤ炭素膜蒸着を行った。成膜温度２５℃。

【００６６】（酸素ガスバリア性）

（ボトル）試作ボトルを真空チャンバー内に入れ、真空減圧した後、高純度窒素ガスを流入させ、ボトル内気相を窒素ガス置換した。その後、ゴム栓にて密封した。酸素濃度２０．９％の３０℃－ＲＨ８０％条件に保存した。３週間後に、ガスタイトシリンジを用い、ボトル内空気を採取し、ＧＣ分析し、ＢＯ$_2$ に換算した。

（延伸シート）Ｍｏｃｏｎ社製ガス透過試験機を用い、４０℃条件下、酸素透過度を測定し、酸素透過係数に換

算した。

【００６７】（機械的強度）

（ボトル）金型ブローボトルと炭素薄膜を蒸着後のボトル胴部（横方向）に１０mmφのジグを用い、ひずみ量１０％の圧縮ひずみ試験を行った。ひずみ変形時に胴部方向で割れが生成したボトルを×とし、変形時に割れの生じないボトルを○とした。

（延伸シート）二軸延伸シートを用いた、延伸軸方向（X，Y）を軸とする方向、及び、延伸二軸のなす対角方向（４５°）を軸とする方向にそれぞれＡＳＴＭ－１８２２型ダンベルを切り出し、ＯＲＩＥＮＴＥＣ社製引っ張り試験機にて引っ張り応力－ひずみ曲線を得た。

【００６８】［実施例４］ポリ乳酸を射出成形機を用い、１９０℃～２００℃条件下、口径２８mmφのプリフォームを射出成形した。金型温度１５℃。次に、プリフォームを赤外線ヒーターにて６５℃～７５℃に再加熱後、金型ブロー成形機を用い、５００ml容の平均肉厚３００μmの金型ブローボトルを作成した。この場合、圧縮空気吹き込み口と排気口を併設させ、初期の圧縮空気圧を３０Kg／cm^2 とした後、段階的にブロー時間内に減圧した。最終的なブロー圧力を０．５Kg／cm^2 とした金型ブロー成形を行った。次に、ＣＶＤ蒸着装置にて、ボトル形状の電極とボトル内部に設置した電極を用い、ボトル内圧力を真空減圧後、ヘキサン・アルゴン混合ガスを原料ガスとする、成膜圧０．１ｔｏｒｒ、高周波電力１３．５６ＭＨｚのＰＥ－ＣＶＤ炭素膜蒸着を行った。成膜温度２５℃。炭素膜を蒸着後のボトルを酸素濃度２０．９％の４０℃－ＲＨ８０％に保存して得たＢＯ$_2$ を得た。更に、ボトル胴部（横方向）に１０mmφのジグを用い、ひずみ量１０％の圧縮ひずみ試験を行った。ひずみ変形時に胴部方向で割れが生成したボトルを×とし、変形時に割れの生じないボトルを○とした。得られた結果を表４に示した。

【００６９】［比較例５］ポリ乳酸を射出成形機を用い、１９０℃～２００℃条件下、口径２８mmφのプリフォームを射出成形した。金型温度１５℃。次に、プリフォームを赤外線ヒーターにて６５℃～７５℃に再加熱後、金型ブロー成形機を用い、５００ml容の平均肉厚３００μmの金型ブローボトルを作成した。この場合、圧縮空気吹き込み口と排気口を併設させ、初期の圧縮空気圧を３０Kg／cm^2 とした後、段階的にブロー時間内に減圧した。最終的なブロー圧力を０．５Kg／cm^2 とした金型ブロー成形を行った。上記ボトルを窒素置換後、酸素濃度２０．９％の３０℃－ＲＨ８０％に保存して得たボトルのＢＯ$_2$ を得た。更に、ボトル胴部（横方向）に１０mmφのジグを用い、ひずみ量１０％の圧縮ひずみ試験を行った。ひずみ変形時に胴部方向で割れが生成したボトルを×とし、変形時に割れの生じないボトルを○とした。得られた結果を表４に示した。

【００７０】［比較例６］ポリ乳酸を射出成形機を用い、１９０℃～２００℃条件下、口径２８mmφのプリフォームを射出成形した。金型温度１５℃。次に、プリフォームを赤外線ヒーターにて６５℃～７５℃に再加熱後、金型ブロー成形機を用い、５００ml容の平均肉厚３００μmの金型ブローボトルを作成した。この場合、圧縮空気圧力を３０Kg／cm^2 の一定圧とした金型ブロー成形を行った。次に、ＣＶＤ蒸着装置にて、ボトル形状の電極とボトル内部に設置した電極を用い、ボトル内圧力を真空減圧後、ヘキサン・アルゴン混合ガスを原料ガスとする、成膜圧０．１ｔｏｒｒ、高周波電力１３．５６ＭＨｚのＰＥ－ＣＶＤ炭素膜蒸着を行った。成膜温度２５℃。炭素膜を蒸着後のボトルを酸素濃度２０．９％の３０℃－ＲＨ８０％に保存して得たボトルのＢＯ$_2$ を得た。更に、ボトル胴部（横方向）に１０mmφのジグを用い、ひずみ量１０％の圧縮ひずみ試験を行った。ひずみ変形時に胴部方向で割れが生成したボトルを×とし、変形時に割れの生じないボトルを○とした。得られた結果を表４に示した。

【００７１】［実施例５］ポリ乳酸を押し出し機を用い、スクリュー部のＣ１～Ｃ４温度を１９０℃～２００℃、Ｔダイ温度を１９０℃とした、２００mm幅、２mm厚のシートを成形した。その後、加熱オーブンを用い、６５℃～７５℃に再加熱し、改造したテンター式二軸延伸機を用い、３×３倍の二軸延伸を行った（平均肉厚：２００μm）。この場合、初期の延伸速度を１０m／ｍｉｎとし、所定の延伸倍率に至るまでに延伸速度を０．０５m／ｍｉｎに段階的に減速した。次に、真空チャンバー内上下に設定した平板電極を用い、ヘキサン・アルゴン混合ガスを原料ガスとした、成膜圧０．１ｔｏｒｒ、高周波電力１３．５６ＭＨｚのＰＥ－ＣＶＤ炭素膜蒸着を行った。成膜温度２５℃。更に、Ｍｏｃｏｎ社製ガス透過試験機を用い、４０℃条件下、酸素透過度を測定し、酸素透過係数に換算した。更に、延伸軸方向（X，Y）を軸とする方向、及び、延伸二軸のなす対角方向（４５°）を軸とする方向にそれぞれＡＳＴＭ－１８２２型ダンベルを切り出し、ＯＲＩＥＮＴＥＣ社製引っ張り試験機にて引っ張り応力－ひずみ曲線を得た。得られた結果を表５に示した。

【００７２】［比較例７］ポリ乳酸を押し出し機を用い、スクリュー部のＣ１～Ｃ４温度を１９０℃～２００℃、Ｔダイ温度を１９０℃とした、２００mm幅、２mm厚のシートを成形した。その後、加熱オーブンを用い、６５℃～７５℃に再加熱し、改造したテンター式二軸延伸機を用い、３×３倍の二軸延伸を行った（平均肉厚：２００μm）。この場合、初期の延伸速度を１０m／ｍｉｎとし、所定の延伸倍率に至るまで延伸速度を０．０５m／ｍｉｎに段階的に減速した。上記延伸シートを用い、Ｍｏｃｏｎ社製ガス透過試験機を用い、４０℃条件下、酸素透係数を測定し、酸素透過係数に換算した。更に、延伸軸方向（X，Y）を軸とする方向、及

び、延伸二軸のなす対角方向（４５°）を軸とする方向にそれぞれＡＳＴＭ－１８２２型ダンベルを切り出し、ＯＲＩＥＮＴＥＣ社製引っ張り試験機にて引っ張り応力－ひずみ曲線を得た。得られた結果を表５に示した。

【００７３】［比較例８］ポリ乳酸を射出成形機を用い、スクリュー部のＣ１～Ｃ４温度を１９０℃～２００℃、Ｔダイ温度を１９０℃とした、２００mm幅、２mm厚のシートを成形した。その後、加熱オーブンを用い、６５℃～７５℃に再加熱し、改造したテンター式二軸延伸機を用い、３×３倍の二軸延伸を行った（平均肉厚：２００μm）

この場合、延伸速度を１０ｍ／ｍｉｎの一定延伸速度とした。次に、ＣＶＤ蒸着装置にて、ボトル形状の電極とボトル内部に設置した電極を用い、ボトル内圧力を真空減圧後、ヘキサン・アルゴン混合ガスを原料ガスとする、成膜圧０．１ｔｏｒｒ、高周波電力１３．５６ＭＨｚのＰＥ－ＣＶＤ炭素膜蒸着を行った。成膜温度２５℃。上記延伸シートを用い、Ｍｏｃｏｎ社製ガス透過試験機を用い、４０℃条件下、酸素透過係数を測定し、素透過係数に換算した。更に、延伸軸方向（Ｘ，Ｙ）を軸とする方向、及び、延伸二軸のなす対角方向（４５°）を軸とする方向にそれぞれＡＳＴＭ－１８２２型ダンベルを切り出し、ＯＲＩＥＮＴＥＣ社製引っ張り試験機にて引っ張り応力－ひずみ曲線を得た。得られた結果を表５に示した。

【００７４】

【表４】

	実施例 4	比較例 5	比較例 6
ボトル平均肉厚	300 μm	300 μm	300 μm
炭素蒸着膜厚	0.1 μm	-	0.1 μm
酸素バリア性 1)	0.101	0.81	0.101
圧縮ひずみ 10%時のボトル強度	○	×	×

1)：単位，cc/bottle/day

【００７５】

【表５】

	実施例 5		比較例 7		比較例 8	
平均肉厚	200 μm		200 μm		200 μm	
炭素蒸着膜厚	0.1 μm		-		0.1 μm	
酸素バリア性 2)	0.64		32.05		0.64	
延伸速度	勾配 初期 1000mm/min 中期 500mm/min 後期 50mm/min		勾配 初期 1000mm/min 中期 500mm/min 後期 50mm/min		定速 1000mm/min	
延伸倍率	3×3		3×3		3×3	
降伏点強度	MD	45°（対角）	MD	45°（対角）	MD	45°（対角）
	96	91	96	91	95	97
機械的強度の異方性	MD＞45°		MD＞45°		MD＜45°	

2)：単位，$cm^3(STP)/cm^2 \cdot sec \cdot cmHg$

【００７６】

【発明の効果】本発明によれば、初期の延伸速度が大きく且つ終期の延伸速度が小さくする延伸速度に負の勾配を設けた二軸延伸操作を行うことにより、脂肪族ポリエステルの延伸成形物の強度特性が前記式（１）を満足する範囲にあって機械的強度の異方性が解消乃至低減され、しかもこの異方性の改善が配向度（Ｄｏ）が０．１５以上という領域で達成される。本発明の延伸成形体からなる容器は、耐座屈性や耐落下衝撃性に優れていると共に、膨張収縮や変形による割れに対しても有効に防止されている利点を有する。更に、この脂肪族ポリエステル延伸成形体に、化学蒸着法（ＣＶＤ）により硬質炭素膜を形成させることにより、耐気体透過性を向上させ、しかも低分子有機成分の収着をも抑制することができる。

【図面の簡単な説明】

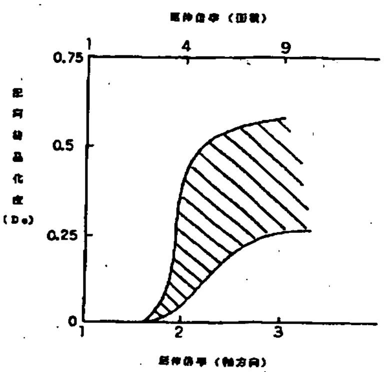
【図１】脂肪族ポリエステル延伸成形体についての各種延伸成形品について得られた延伸倍率（軸方向延伸倍率、面積延伸倍率）と配向結晶化度（Ｄｏ）との関係を示すグラフである。

【図２】無配向の脂肪族ポリエステルの^{13}Ｃ広幅ＮＭＲスペクトルパターンを示した。

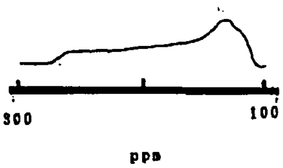
【図３】配向軸とＮＭＲの静磁場方向とが直角方向になる場合の脂肪族ポリエステルの[1][3]Ｃ広幅ＮＭＲスペクトルパターンを示した。

【図４】配向軸とＮＭＲの静磁場方向とが平行方向にした場合の脂肪族ポリエステルの[1][3]Ｃ広幅ＮＭＲスペクトルパターンを示した。

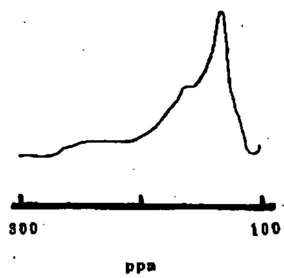
【図１】



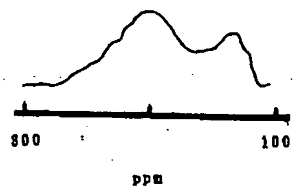
【図２】



【図３】



【図４】



フロントページの続き

(51)Int.Cl.[7]	識別記号	ＦＩ	ﾃｰﾏｺｰﾄﾞ(参考)
Ｂ２９Ｌ　7:00			
9:00			

Ｆターム(参考)　3E033 AA08 BA17 BB04 BB05 BB08
EA10 FA02 FA03 GA02 GA03
4F100 AA37B AA37C AK41A BA02
BA03 BA06 BA10A BA10B
BA10C EH66B EH66C EH662
EJ38 EJ381 GB16 JA05A
JA11A JC00 JD02 JK02A
JK10 JK20 JM02B JM02C
YY00A
4F208 AA24C AE01 AG01 AG03
AG07 LA02 LB01 LN28
4F210 AA24C AE01 AG01 AG03
AG07 AR08 QC05 QC07 QD25
QG01 QG18